CHAPTER -1

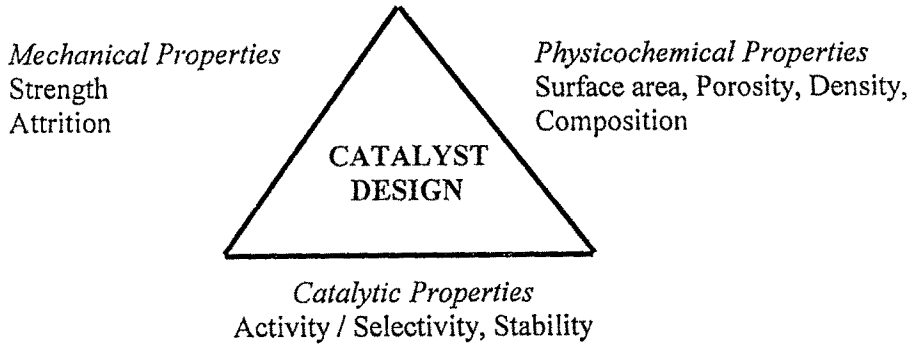
INTRODUCTION

1.0 INTRODUCTION

1.1 Catalysis and Industry

The modern industrialized world would be inconceivable without 'catalysts'. An important task of catalysts is to lower the raw material and energy requirement of chemical reactions. A major target in catalyst development is to obtain high yields in conjunction with high selectivity. The elimination of side products saves raw materials and reduces pollution. It also leads to energy savings in separation processes such as distillation and extraction. The importance of catalysis in chemical industry is evident from the fact that 75% of all chemicals are produced with the aid of catalysts and in newly developed processes, the figure is over 90%. In this context, research directed towards the design and development of new catalysts has become an area of intense interest.

Catalyst preparation is considered to be a black art. The synthesis of catalyst involves an optimized combination of interdependent mechanical, physicochemical and catalytic properties. A triangular concept of catalyst design introduced by Richardson is shown below:



Catalysts can be gases, liquids or solids. Most of the industrial catalysts are liquids or solids. The suitability of a catalyst for an industrial process depends mainly on three properties viz. Activity, Selectivity and Stability.

In recent years, a number of homogeneously catalyzed industrial processes have been brought on stream. The high selectivity of the homogeneous catalysts arising from their molecular nature, mild operating conditions, availability of the metal atoms as catalysts to the substrate and better defined active sites contribute to the higher activity of these catalysts. However, the major disadvantage of homogeneous catalysts is the problem of their separation from the reaction products and recovery for reuse, which is often expensive. Traditionally, the heterogeneous catalysts predominate over their homogeneous counterparts due to their economical and ecological benefits, ease of separation of catalyst from reaction products, recycling efficiency, thermal and mechanical stability, ease of handling in large scale operations over a wide range of reaction conditions etc. The main disadvantage of the heterogeneous catalysts is that they are less selective and require elevated temperatures and vigorous operating conditions. Hence, in order to retain the advantages and overcome the disadvantages of homogeneous and heterogeneous catalysts, the idea of heterogenising a homogeneous catalyst on to a solid support like an inorganic oxide or an organic polymeric support has gained importance. Selected examples of supports and their application in organic reactions are illustrated in **Table 1.1.1.-1.1.3.** Over the past few years a large number of reviews have appeared on solid supported catalysts and their applications in organic reactions [16-22] .

Table 1.1.1. Classes of Supports

INORGANIC	ORGANIC
Silica	Polystyrene
Zeolites	Polyvinyl pyridine
Clays	Polyvinyl alcohol
Metal oxides	Poly amino acids

Table 1.1.2. Metal complexes immobilized on inorganic supports

Reaction	Metal complex/support	References
Olefin Metathesis	$Mo(CO)_6/Al_2O_3$	1
Catalytic Reforming	$Re_2(CO)_{10}/ Al_2O_3$ (impregnated with Pt)	2
Benzene Hydrogenation	$Ni(CO)_4$/MX Zeolite	3
CO Reduction	$Fe(CO)_{12}/SiO_2$	4
Olefin Oligomerisation	$Ni(CO)_4/\gamma$- Al_2O_3	5

Table 1.1.3. Metal complexes immobilized on organic supports

Reaction	Metal complex	Polymer	Substrate	Ref
Hydrogenation	$RhCl(PPh_3)_3$	Phosphinated poly(S-DVB)	Cyclohexene	6
	K_2PdCl_4	Amberlyst A 27	Styrene	7
Hydroformylation	$Rh(acac)(CO)_2$	Phosphinated Amberlyst XAD-2	Hex-1-ene	8
Hydrosilylation	$Pd(PhCN)_2Cl_2$	Amberlyst A21 with Me_3SiOH	Butadiene	9
Oxidation	$FeCl_2 \cdot 4H_2O$	Poly(4-vinylpyridine)	Cyclohexane	10
	Mn(Salen)	Janda Jel	Cis-β-methylstyrene	11
	$MoO_2(acac)_2$	Poly(benzimidazole)	Cyclohexene	12
	Mn(Salen)Cl	Poly(methyl-methacrylate)	1-phenylcyclo-hexene	13
Isomerisation	Co(II)porphyrin	Polystyrene	Quadricyclane	14
Polymerisation	$Co(acac)_2$	Polyvinylimidazole	Butadiene	15

1.2 Polymer supported catalysts

The development of environmentally benign synthesis has evoked a renewed interest in developing polymer-bound metal catalysts and reagents for organic synthesis that maintain high activity and selectivity[23-25] . The immobilization of transition metals on polystyrene supports offers a number of advantages over traditional solution phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration. They do not contaminate the product solution, they can be recycled, and they can help to increase selectivity. As transition metal complexes are often expensive to purchase or prepare, the immobilization on a support, thereby enabling simple extraction and recyclablity, makes for commercial advantage as well as ease of manipulation. There are however a number of disadvantages including the fact that leached costly metals are often not recyclable. In addition, when considering asymmetric synthesis, the enantioselectivity of polymer supported complexes can be less than that of the homogeneous analogue. As a result, much recent work has been focused on developing and screening new ligand derivatized polystyrene supports for attachment of metals and on developing methods for increasing activity and selectivity. Supported catalysts have also been used for rapid production of compound libraries[26] . Also, there has been an increase in reports presenting the use of combinatorial methods to discover new catalysts, as discussed recently in several reviews [27-29] .

Merrifield's resin (chloromethylated styrene-divinyl benzene copolymer) has been the widely used macromolecular support for functionalization and subsequent complexation with various metal ions. Such supported complexes have been employed

to catalyze organic reactions (**Table 1.2.1.**). Ligands which have been commonly anchored to polystyrene prior to complexation with metal ions include dipyridylamine [38], phosphines [39], β-diketones [40], Schiff bases [41] and multidentate amines [42]. Anchoring of N,O containing ligand such as an α-amino acid directly on a polymer backbone has not been well studied. One of the major problems associated with binding of optically active amino acids is the presence of reactive amino and carboxylic groups. Synthetic sequence commonly involves protection-deprotection strategy of the desired end group to overcome racemization and separation problems which are in addition sensitive to pH of reaction medium. One of the earliest instance of an α-amino acid supported Merrifield's resin was reported by Petit *et al.* [43]. This study describes the methods for preparation of Cu(II) complexes with different polymer bound amino acids. Catalytic activity, however, was not investigated. More recently zeolite encapsulated copper(II)-histidine complexes were shown to exhibit catalytic activity in the oxidation of olefins and alcohols with high turnovers [44]. The interest in these complexes stems from the fact that metal-amino acids resemble the active center of metal-enzymes, which are known to participate in selective catalytic oxidation reaction in nature [45,46].

In continuation of our work on the catalytic application of bidentate Schiff base (N,O donor) bearing polymer supported catalysts [47,48] we have in the present work devised a convenient synthetic strategy for anchoring of potentially bidentate amino acids such as L-valine & L-phenyl alanine on moderately cross-linked chloromethylated poly(styrene-divinyl benzene) support followed by isolation of the corresponding metal (Mn, Cu, Ru & Pd) complexes.

Table 1.2.1. Reactions using polystyrene supported transition metal complexes

Reaction	Substrate	Catalyst	Ref
Hydrogenation	Cycloocta 1,3-diene	Chloromethylated crosslinked polystyrene supported titanocene	30
	Cyclohexene	8% crosslinked polystyrene supported [$Rh(CO)_2$ pentane-2,4 dione]	31
	Nitrobenzene	Chloromethylated 8% poly(styrene-divinylbenzene) supported Pd(II)-(L) -2 aminobutanol	32
Olefin metathesis	*cis* 2-pentene	Poly(styrene-divinylbenzene)supp-orted $Cl_2(PR_3)_2Ru{=}CH\text{-}CH{=}CPh_2$	33
Isomerisation	Quadricyclane	Polystyrene supported Pd(0) bipyridyl	34
Oxidation	Cyclohexene	Polystyrene supported Phospho-tungstic complex	35
	Cyclohexene	Polystyrene supported 2,2'-bipyridine $NiCl_2$ complex	36
	Cyclohexene	Polystyrene supported $MoO_2(acac)_2$ and $VO(acac)_2$	37
	cis-β-methyl-styrene	Polystyrene supported Mn(Salen) complex	11

These newly synthesized compounds have been evaluated as catalysts for the epoxidation/oxidation of alkanes, alkenes & alcohols in presence of *tert*-butyl hydroperoxide as the oxidant under mild conditions and also the reduction of alkenes, nitro compound & ketones using a source of high pressure hydrogen. The effect of different reaction parameters on the kinetics of oxidation/reduction has been examined in detail. A brief study on the recyclablity of supported catalysts has been undertaken.

1.3 Asymmetric synthesis and polymer supported catalysts

Many molecules appear in two chiral forms that mirror each other. In nature *one* of the forms is often dominant, and in our cells one fits 'like a glove' on receptor sites, in contrast to the *other*, which may even be harmful. Pharmaceutical products are now increasingly available in their chiral form, and the difference between the two forms can be a matter of life and death, for example, in the thalidomide disaster in the 1960s. That is why it is vital to be able to produce the two chiral forms separately. However, despite the high turnover numbers that naturally occurring enzymes achieve, all cellular machinery is subject to degradation and must be regenerated by biosynthesis. This poses to chemists the irresistible challenge of doing one better than Nature, namely, ***'immortal'*** catalysts that do not deactivate and can be recovered with efficiencies of 100%. While this is clearly an unattainable goal, the present work highlights the attempts that were made to asymptotically approach it.

There is now a strong demand for efficient methods for asymmetric syntheses, the technique that allows facile production of one form versus the other and finding new methods has in the past few years become a key activity for organic chemists for converting *pro*-chiral substrates into chiral products with high enantioselectivity. Such reactions are highly productive and economical, and obviate the need to treat or convert waste resulting from racemate resolution. The demand for chiral chemicals including merchant sales & captive/contract production is already in excess of $9.6 bn and will increase @9.4% annually to $15 bn in 2005 (**Table 1.3.1.**), driven largely by pharmaceuticals where regulations will compel a shift to optically pure isomers.

Table 1.3.1. US demand for chiral chemicals

	Year 2000	Year 2005	Annual growth (%)
Chiral chemicals	9.64	15.11	9.4
a. Pharmaceutical chemicals	6.84	11.45	10.9
* Hormones & related products	1.52	2.60	11.4
* Anti-infectives	1.43	2.13	8.2
* Cardiovasculars	1.18	1.75	8.2
* Central Nervous System	0.92	1.35	8.1
* Respiratory	0.65	1.31	15.1
* Others	1.13	2.29	15.2
b. Non-pharmaceutical chemicals	2.80	3.66	5.5

[Billion US $] Source: Chemical weekly

The development of catalytic asymmetric synthesis has been highlighted by the recent Nobel Prize in Chemistry(2001) awarded jointly to William S. Knowles (US) and Ryoji Noyori (Japan) for their work on chirally catalyzed hydrogenation and Barry Sharpless (Scripps Research Institute, California) for his work on chirally catalyzed oxidation reactions.

These scientists developed molecules (*also* chiral) that can catalyze important reactions so that only one of the two mirror image forms is produced. Knowles, for instance, discovered that it was possible to use transition metals to make chiral catalysts

for hydrogenation, a work that led to the development of an industrial process (plant in operation since 1974) for production of the drug L-DOPA, which is used in the treatment of Parkinson's disease. Noyori led the further development of this process to today's general chiral catalysts for hydrogenation. Sharpless on the other hand, has pioneered the development of chiral catalysts for another important type of reaction *i.e.* 'oxidation'.

Discovery of the BINAP-Ru(II) complex catalysts by Noyori was a major advance in stereo-selective organic synthesis. These chiral Ru complexes serve as catalyst precursors for the highly enantioselective hydrogenation of a range of α,β- and β,γ-unsaturated carboxylic acids and for converting β-keto carboxylic esters in to β-hydroxy easters in high (up to 100%) enantiomeric purity. This entirely chemical approach is far superior to biological versions, including bakers' yeast reduction, where efficiency is often variable. This transition metal catalysis is clean, simple and economical to operate and hence is capable of conducting a reaction on any scale from <100 mg to >100 kg with a very high (up to 50%) substrate concentration in organic solvents. This asymmetric hydrogenation method is utilized in academic and industrial research laboratories to develop pharmaceuticals, agrochemicals, flavours and fragrances. The anti-inflammatory agent (S) – Naproxen, for example, is produced in high yield and high enantiomeric excess using Noyori's catalyst.

Parallel to the progress in catalytic asymmetric hydrogenation, Sharpless asymmetric epoxidation is now a vital part of industrial processes for ton-scale productions of epoxy alcohols such as (S)- & (R)-glycidol and methylglycidol, which are versatile building blocks for the synthesis of a number of chiral molecules.

Despite the fact that hundreds of new chiral ligands and their transition metal complexes have been reported, and many of them are known to be highly effective in the asymmetric formation of C-H, C-C, C-O and C-N bonds, etc. only a few systems have been developed into industrial processes. At present, most chiral synthons are still produced from natural chiral building blocks or through the resolution of racemic mixtures. The lack of application of homogeneous asymmetric catalysis is party due to the problems of separation and recycling of the expensive chiral catalysts. To facilitate the separation of the chiral catalysts from the reaction mixture, methods for immobilizing the homogeneous catalyst have been actively pursued (**Table 1.3.2.**). In recent years, studies have been carried out for the design and synthesis of recoverable catalysts for asymmetric organic synthesis [55,56].

Table 1.3.2. Asymmetric synthesis using polystyrene supported metal complexes

Reaction	Substrate	Catalyst	Reference
Epoxidation	Alkene	PS supported manganese porphyrins	49
		PS supported ruthenium porphyrins	50
		PS supported Mn Salen complex	51
Hydrogenation	Alkenes & β-keto esters	PS supported ruthenium BINAP complex	52
	Ketones	PS supported ruthenium BINAP complex	53
	Ketones	Styrene & DVB copolymer resin functionalized with oxazaborolidine	54
Hydroformylation	Olefin	Polymer supported Pt complex	57
Alkylation	Aldehyde	Polystyrene supported catalyst	58
Michael addition	Unsaturated ketone	Supported catalyst	59

In particular, the asymmetric epoxidation of olefins constitutes one of the most powerful methods in the synthesis of enantiomerically pure compounds. Epoxides are versatile synthetic intermediates that can be readily converted into a large variety of useful compounds by means of regioselective ring opening[60]. The design and development of catalysts that can lead to enantioselectivity in the epoxidation of unfuctionalized olefins represents a major challenge in asymmetric synthesis[61-63]. Some of the promising catalyst systems for the asymmetric epoxidation of unfuctionalized olefins involve chiral porphyrins [64,65] and chiral salen-complexes developed by Jacobsen[66-67] , Katsuki[68-69] and others[70,71]. In the case of chiral Mn(III) salen systems stereo-control and enantioselectivity were shown to depend on the trajectory of approach of the alkene to the catalytically active oxo-Mn(V) intermediate. The tendency for formation of inactive μ-oxo Mn(IV) dimer during the catalytic cycle limits the application for recycling. This lead to the development of chiral complexes immobilized on inorganic and polymeric supports [72-75]

It has been recognized that asymmetric epoxidation of simple straight chain terminal olefins is difficult. Though a great deal of success has been achieved in asymmetric epoxidation of specific substrates such as acyclic olefins, styrene and *cis/trans* alkenes, not much work has been reported on simple terminal aliphatic olefins [64,76,77] .

Aim and objective of the work

The aim of the present work is to (a) Synthesize an α-amino acid liganded polymeric support (b) Synthesize polymer supported transition metal complexes of Mn(II), Cu(II), Ru(III) and Pd(II) using amino acid liganded polymer (c) evaluation of catalytic activity in the epoxidation, oxidation and hydrogenation reaction as well as in asymmetric synthesis.

The present study includes:

(1) Use of a simple synthetic strategy for anchoring an optically active amino acid to chloromethylated poly(styrene-divinyl benzene) resin followed by complexation with metal ions such as Mn(II), Cu(II), Ru(III) and Pd(II) to obtain the polymer supported catalysts. A series of catalysts with different cross linking (6% & 8%) and different amino acids (L-Valine & L-Phenyl alanine) as ligands were prepared.

(2) Characterization of catalysts by physicochemical methods such as surface area, pore volume, apparent bulk density, swelling behaviour, chemical analysis, IR, UV-Vis, DRS, ESR, TGA and SEM.

(3) Investigation of the catalytic behaviour of the newly synthesized catalysts for the

(I) Epoxidation of olefins and oxidation of alkanes.

(II) Hydrogenation of alkenes, carbonyl and nitro compound.

(III) Asymmetric epoxidation of straight chain unfuctionalized olefins.

(IV) Asymmetric reduction of acetophenone.

(4) Catalyst life cycle studies.

(5) Investigation of the probable mechanistic pathways for epoxidation/oxidation and hydrogenation.

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