CHAPTER - I

INTRODUCTION

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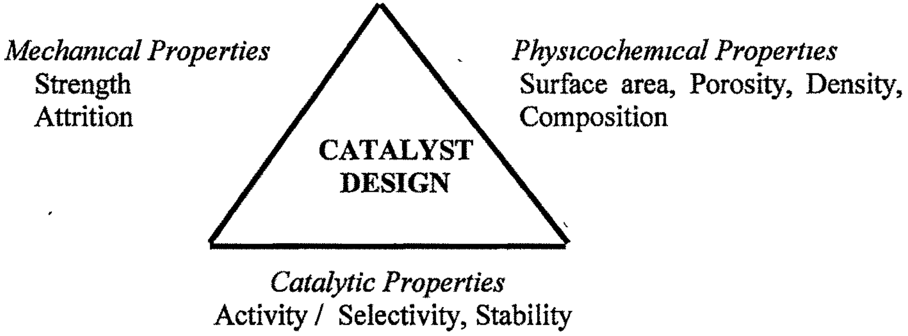
Catalysis is the key to chemical transformations. Most industrial syntheses and nearly all-biological reactions require catalysts. An ideal catalyst is defined as one which is not consumed in a chemical reaction but accelerates the chemical reaction without affecting the position of the equilibrium. In practice, this is not so. Owing to competing reactions, the catalyst undergoes chemical changes, resulting in the lowering in its activity.

The basic inorganic and organic chemical industries constitute a major segment of global economy. Industrial production of various chemicals are based on catalytic processes. The notable among them are catalytic hydrogenation(Sabatier), ammonia synthesis (Haber), fuels and chemicals from synthesis gas(Fischer-Tropsch), catalytic cracking (Houndry, Mobil Oil Co.), polymerization(Ziegler-Natta), methanol synthesis and many processes in the petroleum and petrochemical industry. The use of tailor made catalysts allows the production of desired products with less environmental pollution due to minimization of by-products and a lower energy consumption[1]

Catalyst preparation is considered to be a black art. The catalysts are prepared with an aim to optimize physical, mechanical, chemical and catalytic properties. Thus catalyst design is 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. Catalysts have normally been classified into two broad categories namely :

1. Homogeneous **2. Heterogeneous**

Homogeneous catalysts

These catalysts possess an uniformly active structure (homogeneity) and are generally employed in the same phase as that of the reactants/substrate. In homogeneous catalysts, as all catalyst molecules or atoms are available to the reactants, they have a number of advantages such as high selectivity, control on chemical modifications, the steric environment around the active metal center, ease of investigation of mechanism at the molecular level and mild operating conditions. A major disadvantage associated with homogeneous catalysts is the problem of separating relatively expensive catalysts from the reaction products with separation requiring special or sophisticated treatment. In most instances, the economics of catalyst recovery are unfavorable. Moreover, these catalysts cannot be used at elevated temperatures. Nevertheless, a few commercial processes utilize homogeneous catalysts for the synthesis of specific organic compounds **(Table 1.1)**.

Heterogeneous catalysts

These catalysts are employed in a different phase than that of the reactant/ substrate. Main advantages of these catalysts are their ready separation and recovery from the reaction mixture. These catalysts can be reactivated for subsequent reuse thus increasing their lifetime. They are characterized by durability which make them useful in fixed and fluidized beds, high thermal stability which is important for industrial production for a wide variety of reaction conditions and relative ease of

Table 1.1
Industrial application of homogeneous catalysts

Reaction	Catalyst	Product /Application	Ref
Epoxidation of propylene (ARCO Process)	Mo(VI)	Propylene oxide	2
Dimerization of Ethylene (Alphabutol Process)	$Ti(OR)_4$-$AlEt_3$	1-Butene (Co-monomer in the synthesis of LLDPE)	3
Oxidation of Ethylene (Wacker Process)	$PdCl_2/CuCl_2$	Acetaldehyde	4
Dimerzation of Propylene (Dimersol Process)	$Ni(RCOO)_2$-$AlEtCl_2$	Propylene dimers (motor gasoline)	5
Linear Oligomerization of Ethylene (SHOP Process)	Ni-chelate/$Al_2Et_3Cl_3$	α-olefins (Linear alkyl benzene sulfonates, lubricants)	6
Asymmetric Hydrogenation (Monsanto Process)	$RhCl(PPh_3)_3$	Synthesis of L-Dopa (Used for Parkinson disease)	7

handling in large scale operations. Heterogeneous catalytic oxidation , ammoxidation and oxychlorination are key technologies for the production of bulk chemicals. A number of other reactions such as hydrogenation, isomerisation, dimerization make use of heterogeneous catalysts. Some industrial applications of heterogeneous catalysts are listed in **Table 1.2.**

Though heterogeneous catalysts have certain advantages over homogeneous catalysts they too have certain disadvantages of being less selective (mainly as a result of their heterogeneity of having more than one active site), vigorous reaction conditions and elevated temperatures. These catalysts have low efficiency which is attributed to the ill-defined surfaces as only the metal atoms on the surface sites are accessible and effective in catalysis.

Heterogenized Homogeneous Catalyst

In order to retain the advantages and to overcome the disadvantages of homogeneous and heterogeneous catalysts, the idea of heterogenising a homogenous catalyst has been explored. Heterogenization is generally carried out to a solid support or chemically bound to the support. This class of catalysts are referred to as "Heterogenized Homogeneous Catalyst" wherein the ligand sphere of the metal remain unchanged. The complex attached to the metal are bathed by the solvents and reactants. Mechanistically, they function as if in solution but operate as a separate mobile phase. The study of these catalysts commonly known as "supported or anchored or immobilized" has in recent years gained a lot of attention and is an actively pursued area of current research [11,12]

The main advantages of these catalysts are:-

a) The support may not merely act as an inert backbone but takes a positive role leading to preferred orientation of the substrate at the catalytic sites and thereby promoting selectivity.

Table 1.2
Industrial applications of heterogeneous catalysts

Reaction	Catalyst	Product	Ref.
Propylene epoxidation (Shell Process)	Ti (IV)/ SiO_2	Propylene oxide	8
Ammoxidation of propylene (SOHIO Process)	$Bi_9PMo_{12}O_{52}$ on 50% Silica	Acrylonitrile	9
Dehydrogenation of Ethylbenzene	Fe_2O_3/ Cr_2O_3 : K_2CO_3	Styrene	10
Ethylene epoxidation	Ag on α-Al_2O_3	Ethylene oxide	10
Hydrogenation of Benzene	Raney Ni	Cyclohexane	10
Polymerization of Ethylene (Phillips Process)	Cr_2O_3/MoO_3	Polyethylene	10

b) Stereochemistry around the metal ion can be altered in a beneficial way by supporting a metal complex with the help of multidenate ligand.

c) The equilibrium between the metal ion and their surrounding ligand can be altered by supporting a metal complex.

d) By supporting a complex, it is possible to stabilize catalytic activity but normally unstable structures which often arise through site separation that prevents dimerization to form stable inactive species.

e) As organic functional groups are covalently attached to the surface of the crystalline solids or polymers, supported metal complexes exhibit different chemical properties compared to their homogenous analogues.

f) Remarkable high selectivities can be achieved on supporting the metal complex as more than one type of catalytic sites are available.

g) By supporting the metal complex, separation of desired products at the end of the reaction becomes easy.

h) The active catalytic species are protected by attachment of the metal complex to a support against poisons such as water or oxygen.

Hence if full benefits of supporting metal complexes are to be achieved, the ideal catalyst would have the specificity and controllability of the homogeneous type and separability of the heterogeneous system. Thus, heterogenized homogeneous or supported catalysts will be a new class of catalysts for the future.

SUPPORTS USED FOR HETEROGENIZED HOMOGENEOUS CATALYST

In general, supported metal complex catalysts developed comprise of two broad classes:-

1. The metal complex is linked to the support through attachment of one of the ligand in which the environment of metal ion on supporting remains unaltered.

2. The reaction of metal complex with support results in the displacement of the ligands attached to the metal and their substitution by groups that forms the essential part of the support.

For the synthesis of supported catalysts, the following points are to be considered while selecting the support:-

1. Surface area of the support
2. Binding capacity of the support for the ligand under specific reaction conditions

3. Stability of the support
4. Stability of the anchored metal complex on the particular support.
5. Steric requirements of the metal complex on the surface of the support

The materials that are used to support metal complexes are divided into two broad classes (**Table 1.3**)

A. INORGANIC SUPPORTS

Inorganic supports have a better mechanical and thermal stability with reasonable heat transfer properties. They have better control over the diffusion rates in most of the reaction conditions. Inorganic oxide supports possess surface hydroxyl groups which are used for the attachment of metal carbonyls. The active surface groups such as silanol and siloxane bridges react readily with the carbonyls, immobilising them through direct surface bonding[13].Other materials used as supports include magnesium oxide and carbon supports in the form of charcoal or carbon black. In recent times, Zeolites with controlled pore size have gained a lot of importance as inorganic supports[14]. They are a class of aluminosilicates characterised by a high degree of crystallinity, regular well-defined structures and intense electrostatic fields within the pores. They consist of a network of SiO_4 and AlO_4 tetrahedra with different SiO_2/Al_2O_3 ratios in which the (-1) charge on the $AlPO_4$ tetrahedron is compensated by inclusion in the structure of cations such as H^+, NH_4^+, Na^+ and Ca^{+2} thus maintaining electroneutrality. Zeolites exist as A, X, Y, and ZSM-5 forms. The experience in the use of zeolite based catalysts in the petrochemical industry can be applied to the selective organic synthesis of chemical intermediates and fine chemicals as zeolites with their numerous adjustable catalytic properties offer a wide range of possibilities for this purpose. A good example of this fact is the vapour phase Beckmann rearrangement in the synthesis of caprolactam

Table 1.3
Classes of Supports

INORGANIC	ORGANIC
Silica	Polystyrene
Zeolites	Polyvinylpyridine
Clays	Polyvinylalcohol
Metal oxides	Polyaminoacids

Table 1.4
Metal complexes immoblized on inorganic supports

Reaction	Metal Complex/Support	Ref
Olefin Metathesis	$Mo(CO)_6$ / Al_2O_3	16
Catalytic Reforming	$Re_2(CO)_{10}$/ Al_2O_3 (impregnated with Pt)	17
Benzene Hydrogenation	$Ni(CO)_4$/ MX Zeolite	18
CO Reduction	$Fe_3(CO)_{12}$/ SiO_2	19
Olefin Oligomerisation	$Ni(CO)_4$/ γ -Al_2O_3	15

from adipic acid by using H_2O_2 as an oxidant over a Ti-containing MFI-Zeolite TS-1, thus avoiding the use of hazardous and corrosive sulphuric acid and generation of ammonium sulphate, an environmentally unaceptable material as by-product. A number of studies have been reported on the catalytic activity of complexes anchored on inorganic supports and many large scale industrial processes are catalysed by using such materials[15]. A summary of selected studies of metal complexes immoblized on inorganic supports are given in **Table 1.4.**

One of the main drawbacks of using inorganic oxides as support is the leaching of the metal complex catalyst from the support into the solution. Moreover, it has a lower number of active sites per unit weight.

B. ORGANIC POLYMERS AS CATALYTIC SUPPORTS

Polymers as supports play a variety of roles depending on the system. In some cases polymer supports act only as carriers for the appropriate catalyst dispersed on the surface. In other cases, the macromolecular network contains tethered sites in the form of functional groups or ligands of metal complexes and sometimes the catalyst is encapsulated within polymeric membranes, in a way that is reminiscent of enzymatic activity in natural systems. The advantages that have encouraged the use of polymeric supports are:-

1. Polymeric supports are in most cases insoluble, non volatile, less toxic and often recyclable, the properties that are especially attractive in an era of enhanced environmental awareness.

2. Most hydrocarbon polymers are chemically inert, as a result, the support does not interfere with catalytic group.

3. Facile separation can be carried out normally by filtration of the products from the reactants.

4. Polymers can be functionalised easily as per the requirement thus providing a wide range of properties.

The physical properties of polymer vary widely depending on molecular weight, the chemical nature of the monomer or combinations of monomers, the conditions of polymerization which affect the arrangement of the polymer molecules and their interactions with one another. Three major types of polymers are known[20-22].

I. Gellular or microporous polymers

This type of polymer have long strands of polymer molecules that are lightly crosslinked or randomly entangled. These polymers are used in hydrocarbon solvents as soluble support which can be separated at the end of the reaction by precipation or by osmotic procedures such as membrane filtration.

II. Macroreticular or macroporous polymers

These polymers have a carefully controlled regular crosslinking (reticular) which allows a high internal surface area to the polymer. These are made either from styrene using divinylbenzene as the copolymer or from acrylates wherein a donor ligand can be supported within as well as on the surface of the polymer.

III. Proliferous or Popcorn polymers

These polymers are formed spontaneously during the polymerization process producing not only a normal glassy material but also a white, porous, opaque granular material referred to as a "Popcorn". Butadiene/styrene polymerization processes are susceptible to the formation of popcorn polymers.

Anchoring of multidentate ligands to insoluble polymeric supports is a technique now commonly utilized based on the pioneering efforts of Merifield in polypeptide synthesis[22]. There has been an increasing use of polymers as supports in organometallic catalysis which has encouraged the use of functionalised crosslinked polystyrene to support transition metal catalytic species. Among the organic polymers that have been used as supports, poly(styrene-divinylbenzene) is widely used as it can be functionalised easily with a wide range of physical properties with the result that their porosity, surface area and solution characteristics can be altered by varying the degree of crosslinking[23,24].The factors that are to be considered for selecting a polymer support are:-

1. Deactivation of the catalytic species can be prevented on supporting it on to the polymer matrix as the polymer support stabilizes the unstable structure on the surface. For example,a catalytic solution of Wilkinson complex $RhCl(PPh_3)_3$ loses its activity on exposure to air but when the complex is supported on to a polystyrene resin, it can be employed in presence of air without deactivation[25].

2. Dimerization of the catalyst in the reaction mixture may be prevented by isolation of the active sites on the polymer matrix ,thus supported catalyst can be prepared with high dispersion of metal atoms on polymer matrix inorder to achieve optimum reactivity and selectivity.

3. The immobilized catalyst may be viewed as a combination of "soluble part" which bears the catalytic sites and an "insoluble polymeric support" inert towards the substrate. This inertness presupposes minimal steric restriction to substrate and product transport near the active sites.

4. Organic polymer supports offer an opportunity of extra selectivity to the catalyst through the control of diffusion of reactants within the polymer. Diffusion rates in a polymer depends on the porous structure of the polymers.

5. The swelling of the polymer in the solvent used for the reaction is an important factor while selecting a support. For example, when solvents used with polystyrene immobilized catalysts are more polar than benzene, two processes occur (i) pore width decreases due to decreased resin swelling (ii) polar gradients between the bulk solvent and the local environment of the active site are created. This is exemplified by the fact that with a change from pure benzene to 1:1 benzene : ethanol solvent, the rate of hydrogenation for cyclohexene increased by a factor of 2.4. Hence the choice of better swelling agent help to promote activity[26].

6. The degree of crosslinking affects the nature of the catalyst. Polymers with varying degrees in crosslinking from 1% to 20% have been used as supports in the preparation of the catalyst.The increased rigidity may enhance the catalytic activity by limiting the likelihood of interaction between those active centers which tend to dimerise with subsequent deactivation. For example, the stable but catalytically inactive titanocene dichloride complex yields upon reduction an active catalyst for the hydrogenation of alkenes and alkynes but the active species readily polymerize with deactivation. However, when immobilized on a 20% crosslinked polystyrene support, a stable catalyst is obtained which is 25-120 times more active than the unattached complex for cyclohexene hydrogenation[27].

In spite of these advantages, polymeric supports have so far been of limited use in industrial processes, with the exception of the polypeptide synthesis and solid acid catalysis by sulfonated crosslinked polystyrene[28]. The reasons for this situation are due to the remaining problems of polymeric supports which are **(a)** limited chemical stability especially at temperatures above 100°C **(b)** poor mechanical properties **(c)** reactions which are often typical to heterogeneous catalysis are diffusion limited since the active sites are buried inside the crosslinked support **(d)** loss in their activity through leaching of metal from the metal complex anchored onto the support. In view of these drawbacks, recently a large number of systems have been developed and considerable scope now exists for their exploitation in routine synthetic chemistry.

Polymer supported phase transfer catalysts(PSPTC) have been widely used in organic synthesis to minimize the loss of the catalyst[29]. Surface enriched polymer supported phase transfer catalysts using vinyl toluene as a functional monomer was prepared and were found to be effective in dichlorocarbene addition to cyclohexene[30]. A relatively new area of application in which polymer matrices are utilized on industrial scale as supports for enzymes in biocatalyzed processes such as the synthesis of aspartic acid and fumaric acid of lactose free milk, 6-aminopenicillanic acid and conversion of acrylonitrile into acrylamide is rapidly expanding[31]. Some of the reactions catalyzed by polymer supported transition metal complexes are listed in **Table 1.5.**

Organic polymers have been successfully used as polymeric carriers in asymmetric synthesis, a technique in which an optically active compound or a functional group is attached to a macromolecular support which acts as a asymmetric reagent or catalyst in the synthesis[40,41]. Recently, linear polytartarate ester supported Ti(o-*i*Pr)$_4$ have been used as catalysts for asymmetric synthesis of epoxide from *trans*-hex-2-ene-1-ol with ee upto 80% conversion[42]. Moreover, polycarbonate-Fe(CO)$_5$,polymethylmethacrylateFe(CO)$_5$, polyvinylidine fluoride-Fe(CO)$_5$ in DMF composites have been prepared and found to have magnetic recording applications[43].Thus the development of viable polymer bound catalyst for a wide variety of laboratory and industrial applications like development in nuclear chemistry, organic synthesis, waste water treatment, pollution control, hydrometallurgy, polymer drug grafts, preconcentration and recovery of trace metal ions has gained research importance.

LITERATURE SURVEY ON POLYSTYRENE - SUPPORTED CATALYSTS

Polymer anchored transition metal catalysts have been investigated from two points of view, one based on polymer chemistry and the other on catalysis. From the viewpoint of polymer chemistry, a polymer anchored transition metal complex catalyst is basically a functional polymer whereas its catalytic function originates from the transition metal complex component, while the polymeric component assists the complex in its work as an active and selective catalyst[11,12,15,44 -51].

Table 1.5
Metal complexes immobilized on organic supports

Reaction	Metal Complex	Polymer	Substrate	Ref
Hydrogenation	$RhCl(PPh_3)_3$	Phosphinated poly-(S-DVB)	Cyclohexene	25
	K_2PdCl_4	Amberlyst A 27	Styrene	32
Hydroformylation	$Rh(acac)(CO)_2$	Phosphinated Amberlyst XAD-2	Hex-1-ene	33
Hydrosilylation	$Pd(PhCN)_2Cl_2$	Amberlyst A21 with Me_3SiO H	Butadiene	34
Oxidation	$FeCl_2.4H_2O$	Poly(4-vinylpyridine)	Cyclohexane	35
	Mn(Salen)	Janda Jel	*cis*-β-methyl-styrene	36
	$MoO_2(acac)_2$	Poly(benzimidazole)	Cyclohexene	37
	Mn(salen)Cl	Poly(methylmeth-acrylate)	1-Phenylcyclo-hexene	38
Isomerisation	Co(II)porphy-rin	Polystyrene	Quadricyclane	39
Polymerisation	$Co(acac)_2$	Polyvinylimidazole	Butadiene	30

metals from low grade ores[52 -54]. A number of industrial processes are known in which ion-exchange resins based on sulfonated polystyrene have been used as catalysts.They include the synthesis of methyl *tert*-butylether (MTBE), *tert*-amylmethyl ether(TAME), bisphenol -A, methylvinylketone, isoamylene and phenol alkylation[50]. A few examples of polystyrene supported transition metal complexes are listed in **Table 1.6.**

In recent years, considerable interest has been generated in the design, synthesis and use of functionalised polymer with bidentate chelating properties, having operational flexibility and tendency of forming metal bound polymers. Moreover, the main problem of leaching of metal complexes from the polymer matrix, when monodentate or non chelated ligands are used, can be overcome by the use of bidentate or chelating ligands, having nitrogen or oxygen as donor atoms giving a coordinatively stable catalyst with higher activity.

The polymeric supports that have been most commonly used are crosslinked polymers, which are insoluble in most of the solvents. Styrene and divinylbenzene(DVB) are the most frequently used monomers for the synthesis of macromolecular supports, as the aromatic ring in poly(styrene-divinylbenzene) copolymer can be funtionalised as any benzene ring. One of the main routes for the preparation of large variety of supports is chloromethylation, which places the chloromethyl group in the *p*- or *m*-positions of the benzene ring. The chloromethylated styrene-DVB copolymer referred to as Merrifield's resin and designated as Ⓟ - CH_2Cl is one of the most important intermediates for the synthesis of functionalised polymer. A survey of main functional groups that can be prepared starting with Ⓟ - CH_2Cl is given in **Scheme 1.1.**

Scheme 1.1 : Functionalized polymeric supports

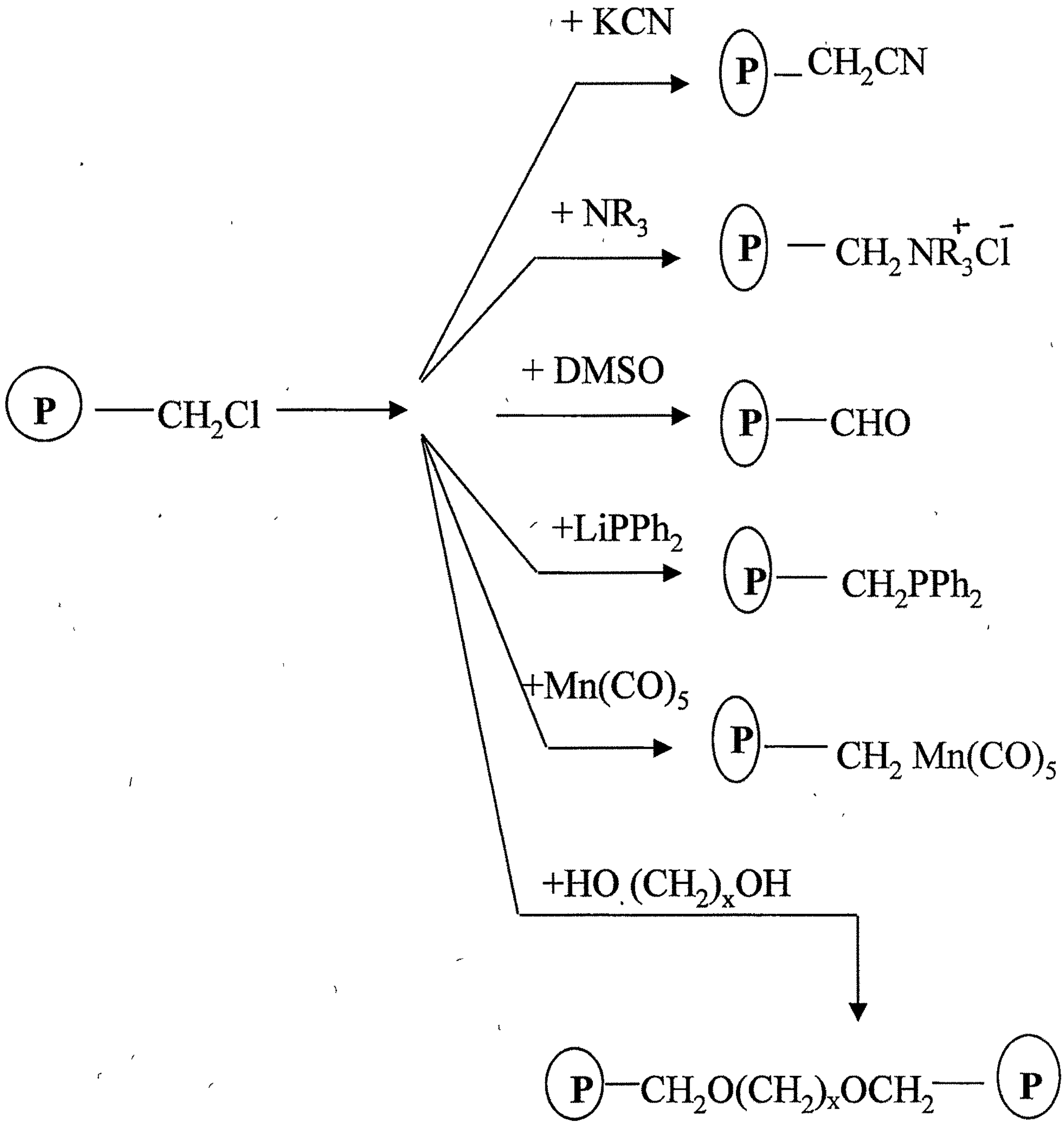


Table 1.6
Reactions carried out using polystyrene supported transition metal complexes

Reaction	Substrate	Catalyst	Ref
Hydrogenation	Cycloocta 1,3-diene	Chloromethylated crosslinked polystyrene supported titanocene	55
	Cyclohexene	8% crosslinked polystyrene supported [Rh(CO)$_2$ pentane-2,4 dione]	56
	Nitrobenzene	Chloromethylated 8% poly(styrene-divinylbenzene) supported Pd(II)-(L) -2 aminobutanol	57
Olefin metathesis	*cis* 2-pentene	Poly(styrene-divinylbenzene)supported $Cl_2(PR_3)_2Ru=CH-CH=CPh_2$	58
Isomerisation	Quadricyclane	Polystyrene supported Pd(0) bipyridyl	59
Oxidation	Cyclohexene	Polystyrene supported Phosphotungstic complex	60
	Cyclohexene	Polystyrene supported 2,2'-bipyridine $NiCl_2$ complex	61
	Cyclohexene	Polystyrene supported MoO_2 (acac)$_2$ and VO(acac)$_2$	62
	cis-β-methyl-styrene	Polystyrene supported Mn(Salen) complex	36

A variety of ligands such as porphyrin derivatives, macrocyclic pyridylamines and Schiff bases have been employed [63-66]. Among them, Schiff bases are one of the most versatile and thoroughly studied ligands but very few reports are available on polymer anchored Schiff bases and their application in catalysis[67-70]. Schiff bases complexed with transition metal are used as catalyst in the selective oxidation ofolefins.Almost all of these catalysts require a monooxygen source such as hydrogen peroxide, *tert*-butylhyroperoxide, sodium hypochlorite, iodosylbenzene etc., to carry out oxygen transfer to the olefins. Symal and Singh [71] have reported the synthesis of Fe(II)-Schiff base complexes of the type "PS-L-$FeCl_2$ .2DMF" by treatment of aminomethylated poly(styrene-divinylbenzene) with salicylaldehyde. Ram and co-workers[72,73] synthesized poly(styrene-divinylbenzene) Pd(II) and Ru(III) complexes using trimethylenediamine[TMDA], glycine, L-2-aminobutanol [L-2AB], ethylenediamine tetraacetic acid[EDTA] and found them to be effective catalysts in the hydrogenation of nitroaromatic compounds and oxidation of olefins under mild reaction conditions.

Direct condensation of an aldehydic group on the polymer backbone with an amine to form the Schiff base have not been reported. Employing this strategy we have prepared polymer supported Schiff base and bidentate ligands containing 'N' donor atoms and subsequently complexed them with Ru(III), Pd(II) and Fe(III) ions. The complexes were evaluated for catalytic activity in the hydrogenation and selective epoxidation of olefins. These reactions are of industrial importance for the synthesis of fine chemicals and pharmaceuticals.

AIM AND OBJECTIVE OF THE WORK

The aim of the present work is to (a) synthesize a Schiff base liganded polymeric support (b) synthesize polymer supported transition metal complexes of Ru (III), Fe(III) and Pd(II) and (c) evaluation of catalytic activity in the

epoxidation and hydrogenation of olefins

The present study includes:-

1. Synthesis of functionalised polymers from chloromethylated poly(styrene-divinylbenzene) by sequential oxidation of chloromethyl group to an aldehydic group, condensation with amines e.g. ethylenediamine and 2-aminopyridine to form the Schiff base functionalised polymer and treatment of functionalised polymer with halides of ruthenium($RuCl_3$), iron($FeCl_3$) and palladium($PdCl_2$) to obtain the polymer supported metal complexes. A series of complexes with different crosslinking (8% and 14%) were prepared.

2. Synthesis of polymer supported ruthenium complexes by direct condensation of chloromethylated poly(styrene-divinylbenzene) having various crosslinks(8% and 14%) with 2-aminopyridine.

3. Characterization of the newly synthesized complexes by physicochemical methods such as surface area, pore volume, apparent bulk density, moisture content, swelling behavior, chemical analysis, infra-red, UV-VIS reflectance, thermogravimetric analysis, morphological study by scanning electron microscopy (SEM) and surface studies by ESCA. The probable structure of the catalysts has been discussed.

4. Investigation of the supported complexes as catalysts in :-

(i) Epoxidation of *cis*-cyclooctene, styrene and cyclohexene using *tert*-butyl hydroperoxide (TBHP) as oxidant using Ru(III) and Fe(III) complexes.

(ii) Hydrogenation of *cis*-cyclooctene using Pd(II) complexes.

5. Catalyst life cycle studies.

6. Investigation of the probable mechanistic pathways for olefin epoxidation and hydrogenation.

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