CHAPTER - 1

INTRODUCTION

1.0 INTRODUCTION

PHENOMENON OF CATALYSIS

Catalysis is the key to chemical transformations Most industrial synthesis and nearly all biological reactions require catalysts Furthermore, catalysis is the most important technology in environmental protection A well-known example is the catalytic converter for automobiles

Catalytic reactions were already used in antiquity, although the underlying principle of catalysis was not recognized at the time. For example, the fermentation of sugar to ethanol and the conversion of ethanol to acetic acid are catalyzed by enzymes (biocatalysts) However, the systematic scientific development of catalysis only began about two hundred years ago, and its importance has grown up to the present day [1]

The term "catalysis" was introduced as early as 1836 by Berzelius in order to explain various decomposition and transformation reactions He assumed that catalysts possess special power that can influence the affinity of chemical substances

A definition that is still valid today is due to Ostwald (1895). "a catalyst accelerates a chemical reaction without affecting the position of the equilibrium "

Ostwald recognized catalysis as a ubiquitous phenomenon that was to be explained in terms of the laws of physical chemistry

Catalysis is a cyclic process the reactants are bound to one form of the catalyst, and the products are released from another, regenerating the initial state The catalytic cycle can be described [2] as shown in **Figure 1**.

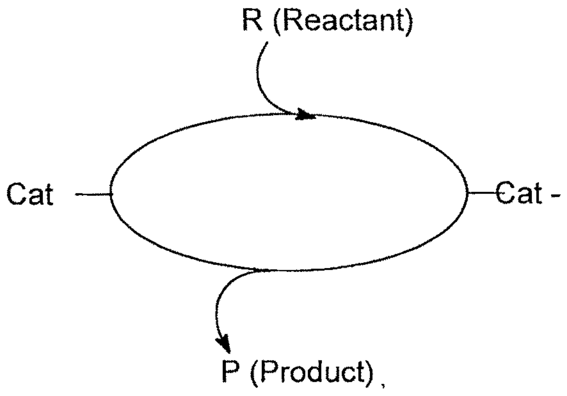


Figure 1 Catalytic cycle

The intermediate catalyst complexes are in most cases highly reactive and difficult to detect

In theory, an ideal catalyst would not be consumed, but this is not the case in practice Owing to the competing reactions, the catalyst undergoes chemical changes, and reactivity becomes lower (catalyst deactivation) Thus catalysts must be regenerated or replaced

Apart from accelerating reactions, catalysts have another important property: they can influence the selectivity of the chemical reactions This means that completely different products can be obtained from a given starting material by using different catalyst systems Industrially, this targeted reaction control is often even more important than the catalytic activity [3].

Most industrial catalysts are liquids or solids. The importance of the catalysts in the chemical industry is shown by the fact that 75% of all chemicals are produced with the aid of catalysts, while newly developed processes, the figure is over 90%. Numerous organic intermediate products required for the production of plastics, synthetic fibers, pharmaceuticals, dyes, crop-protection agents, resins and pigments, can only be produced by catalytic processes

Catalysts have been successfully used in the chemical industry for more than 100 years, examples being the synthesis of sulfuric acid, the conversion of ammonia to nitric acid, and some other developments are catalytic hydrogenation (Sabatir), ammonia synthesis (Haber), fuel and chemicals from synthesis gas (Fischer - Tropsch), catalytic cracking (Houndry, Mobil Oil co), polymerization (Ziegler - Natta), methanol synthesis and many processes involved in the crude-oil processing and petrochemistry, such as purification stages; refining, and chemical transformation, require catalysts Environmental protection measures such as automobile exhaust control and purification of off-gases from the power stations and industrial plants would be inconceivable without catalysts[4].

The use of tailor made catalysts allows the production of desired products with less environmental pollution due to minimization of by-products and lower energy consumption[5] Later developments include new highly selective multicomponent oxide and metallic catalysts, zeolites, and the introduction of homogeneous transition metal complexes in the chemical industry This was supplemented by new high-performance techniques for probing catalysts and elucidating the mechanism of heterogeneous and homogeneous catalysis

The brief historical survey given in **Table 1.1** shows just how closely the development of catalysis is linked to the history of industrial chemistry[6]

MODE OF ACTION OF CATALYSTS

The suitability of a catalyst for an industrial process depends mainly on the following three properties

- **Activity**
- **Selectivity**
- **Stability(deactivation behavior)**

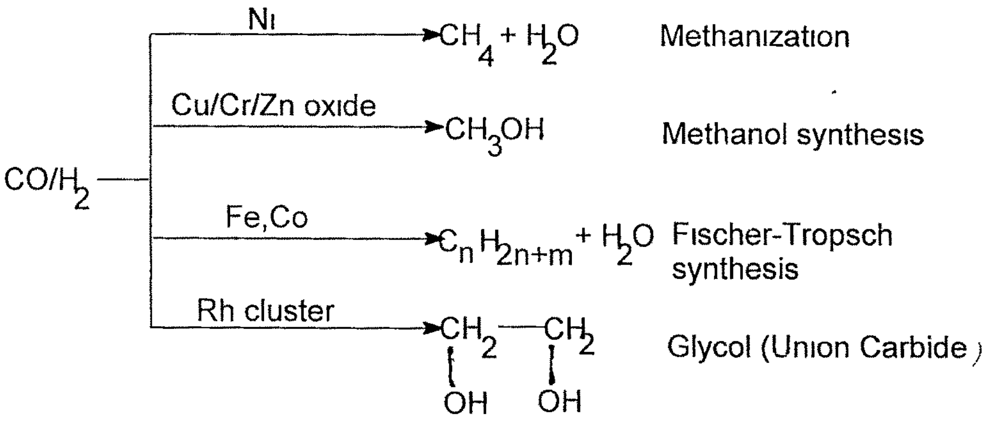
Table 1.1
History of the catalysis of industrial processes [6]

CATALYTIC REACTION	CATALYST	DISCOVERER or COMPANY/YEAR
Sulfuric acid (lead-chamber process)	NO_x	Desormes, Clement 1806
Chlorine production by HCl oxidation	$CuSO_4$	Deacon, 1867
Sulfuric Acid (contact process)	Pt, V_2O_5	Winkler, 1875(BASF)
Nitric acid by NH_3 oxidation	Pt/Rh nets	Ostwald, 1906
Fat hardening	Ni	Normann, 1907
Ammonia synthesis from N_2, H_2	Fe	Mittasch Haber, Bosch, 1908, Production,1913(BASF)
Hydrogenation of coal to hydrocarbons	Fe, Mo, Sn	Bergius, 1913
Oxidation of benzene, naphthalene to MSA or PSA	V_2O_5	Weiss, Downs 1920
Methanol synthesis from CO/H_2	ZnO/Cr_2O_3	Mittasch, 1923
Hydrocarbons from CO/H_2, (motor fuels)	Fe, Co, Ni	Fischer, Tropsch 1925
Oxidation of ethylene to ethylene oxide	Ag	Lefort, 1930
Alkylation of olefins with isobutane to gasoline	$AlCl_3$	Ipatieff, Pines, 1932
Cracking of hydrocarbons	Al_2O_3/SiO_2	Houndry, 1937
Cracking in a fluidized bed	Aluminosilicates	Lewis, Gilliland,1939
Ethylene polymerization,Low-pressure	Ti compounds	Ziegler, Natta, 1954

Oxidation of ethylene to acetaldehyde	Pd/Cu chlorides	Hafner,Smidt(Wacker)
Ammoxidation of propene to acrylonitrile	Bi/Mo	Idol, 1959 (SOHIO Process)
Olefin metathesis	Re, W, Mo	Banks, Bailey,1964
Hydrogenation, isomerization, hydroformylation	Rh-, Ru-complexes	Wilkinson, 1964
Methanol conversion to hydrocarbons	Zeolites	Mobil Chemical Co , 1975
Auto emission	Pt-Rh	1982 [7]
Stack gas	V_2O_5-TiO_2	1982 [7]
Selective oxidation	Ti-silicalites	1988 [7]
Asymmetric synthesis	Cinchonidine-Pt BINAP	1988 [7]
Polymerization	Metallocenes	1991 [7]

Activity . Catalyst activity is determined by measuring the specific rate of the catalyzed reaction in which the desired product forms The specific rate of the catalytic reaction is the rate increase caused by unit quantity (mass, volume, or surface area) of the catalyst compared to the rate of the uncatalyzed reaction

Selectivity: Selectivity is defined as the amount of desired product obtained per amount of consumed reactant A value of selectivity without a conversion is also useless The product of conversion and selectivity is commonly called yield which in short, is the simplest measure of selectivity. The selectivity is of great importance in industrial catalysis, as demonstrated by the example of synthesis gas chemistry, in which, depending on the catalyst used, completely different reaction products are obtained **(Scheme 1).**



Scheme 1: Reactions of synthesis gas

Stability: The chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors Catalyst stability is influenced by numerous factors, including decomposition, coking, and poisoning Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of a process

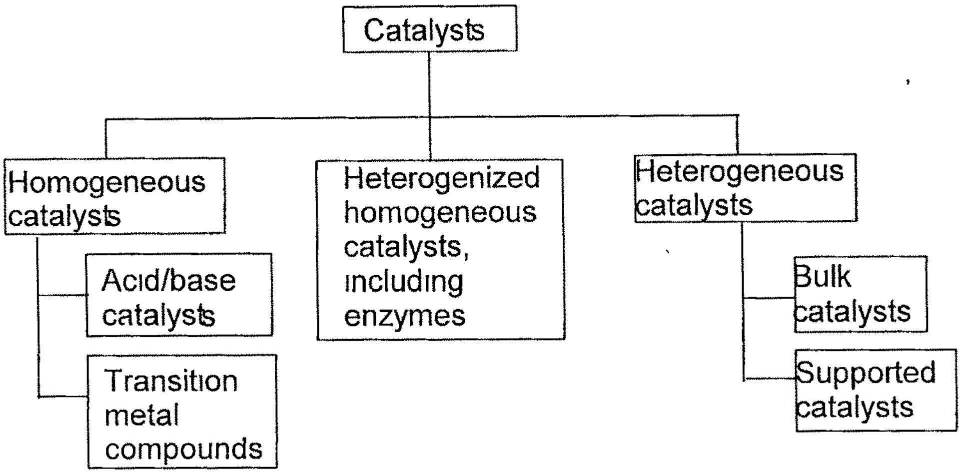
1.1 CLASSIFICATION OF CATALYSTS

Catalysts can be broadly classified into two types

(1) Homogeneous catalysts

(2) Heterogeneous catalysts (solid-state catalysts)

There are also intermediate forms such as homogeneous catalysts attached to solids which are called heterogenized homogeneous catalysts They are also known as immobilized catalysts The well-known biocatalysts(enzymes) also belong to this class.**(Scheme 2)**



Scheme 2 : Classification of catalysts

1.1.1 HOMOGENEOUS CATALYSTS

Catalytic processes that take place in a uniform gas or liquid phase are classified as homogeneous catalysts Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which together with the reactants are molecularly dispersed in the reaction medium They have a number of advantages such as high selectivity, controllability resulting in ready chemical modifications, control of the electronic and 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 the homogeneous catalyst is the problem of separating relatively expensive catalyst from the reaction products The separation requires 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 synthesis of specific organic compounds **(Table 1.2)**

1.1.2 HETEROGENEOUS CATALYSTS

These catalysts are employed in a different phase than that of the reactant Generally the catalyst is solid, and the reactants are gases or liquids Main advantages of these catalysts are their ready separation and recovery of the catalysts from the reaction mixture Solid catalysts are rarely corrosive Strongly exothermic and strongly endothermic reactions are routinely carried out with solid catalysts These catalysts can be reactivated for subsequent reuse thus increasing their life time They are characterized by durability which make them useful in fixed and fluidized bed, high thermal stability which is important for industrial production for a wide variety of reaction conditions and relative ease of 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, dimerisation make use of heterogeneous catalysts **(Table 1.3)**

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 type of active site), vigorous reaction conditions and elevated temperatures These catalysts have lower efficiency which is attributed to ill-defined surfaces as only the metal atoms on the surface sites are accessible and effective in catalysis.

1.1.3 HETEROGENIZED HOMOGENEOUS CATALYSTS

In order to retain the advantages and to overcome the disadvantages of homogeneous and heterogeneous catalysts, the idea of heterogenising a homogeneous 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 remains unchanged The complex attached to the metal are bathed by the solvents and reactants Mechanistically, they function as if in solution but operates as a separate mobile phase These catalysts are also known as “supported or anchored or immobilized catalysts” have in recent years gained a lot of attention and is an actively pursued area of research [22-29]

The main advantages of these catalysts are

1. The support may not be merely an inert back bone. It may take a positive role leading to preferred orientation of the substrate at the catalytic site and so promoting selectivity

Table 1.2
Industrial application of homogeneous catalysts

REACTION	CATALYST	REF.
1 Wilkinson Hydrogenation (a) Cyclohexene→Cyclohexane (b) Styrene→Ethyl benzene	$RhCl(PPh_3)_3$	[8,9]
2. Chiral Hydrogenation.(Synthesis of L-Dopa) (Monsanto process)	$RhCl(PPh_3)_3$	[10]
3 Methanol Carbonylation Methanol→Acetic acid	$Rh(CO)_2I_2$ & CH_3I	[11]
4 Olefin Hydroformylation (Oxo process)	$[HCo(CO)_4]$ Complex	[12]
5 Epoxidation of propylene. (ARCO process)	Mo(VI)	[13]
6 Dimerization of Ethylene (Alphabutol process)	$Ti(OR)_4$-$AlEt_3$	[14]
7 Oxidation of Ethylene Ethylene→Acetaldehyde	$PdCl_2\backslash CuCl_2$	[15]
8 Dimeratization of propylene (Dimersol process)	$Ni(RCOO)_2$- $AlEtCl_2$	[16]
9 Linear Oligomerization of ethylene Ethylene→ α-Olefins (SHOP process)	$Ni(OR)_2$ /Al_2- Et_3Cl_3	[17]

Table 1.3
Industrial application of heterogeneous catalysts .

REACTION	CATALYST	REF.
Propylene epoxidation(Shell process)	Ti(IV)\ SiO_2	[18]
Paraffin hydrocracking	Pd supported on zeolite	[19]
Ammoxidation of propylene (SOHIO process)	$Bi_9PMo_{12}O_{52}$ on 50% Silica	[20]
Dehydrogenation of Ethyl benzene	Fe_2O_3 \ Cr_2O_3 \ K_2CO_3	[21]
Ethylene epoxidation	Ag on α-Al_2O_3	[21]
Hydrogenation of Benzene	Raney Ni	[21]
Polymerization of Ethylene. (Phillips process)	Cr_2O_3 \ MoO_3	[21]

2. The catalysts can be separated easily from the reacting system and can be reused

3. The polymer supported catalysts can be used conveniently in excess when necessary unlike homogeneous catalysts where solubility of the complex would be a limiting factor

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

5. Attachment of a metal complex to support can sometimes provide protection to the catalytic species against poisons such as water or atmospheric oxygen

6. As organic functional groups are covalently attached to the surface of the crystalline solid or polymer, supported metal complexes exhibit different chemical properties from their homogeneous analogues.

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

8. In large scale production process, problems arise from strong corrosive attack on the reactor which can be overcome by the use of anchored catalysts.

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

10. These catalysts provide the possibility of automation in the case of repetitive stepwise synthesis and the facility of carrying out the reaction in a flow reactor on the commercial scale

Hence, if full benefits of supported 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 catalysts of choice for the future

3.1.4.1 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 ligands 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 support

In order to synthesize the heterogenized homogeneous catalysts, the following points are to be considered while selecting the support .

1. The surface area of the support to which the metal complex is to be attached.

2. The capacity of the specific support to bind the ligand functionality itself to the surface under the specific reaction conditions to which the metal complex will be exposed during the application as a heterogeneous catalyst

3. The stability of the support under catalyst reaction conditions or during any catalyst regeneration step.

4. The stability of the anchored metal complex itself on a particular support and the conditions of application

5. The steric requirements of the metal complex on the support surface

1.2 TYPES OF SUPPORTS:

Mainly two types of supports have been used to synthesize the supported metal complex catalysts **(Table 1.4)**

(1) Inorganic oxides and

(2) Organic polymers

1.2.1 INORGANIC OXIDES AS SUPPORTS

The inorganic supports that have been mainly used include silica, alumina, glasses, clays, metal oxides and zeolites [30] These inorganic supports have better mechanical and thermal stability with reasonable heat transfer properties Inorganic substrate also have better control over the diffusion rate in most of the reaction conditions [31] Inorganic oxide supports possess surface hydroxyl groups which are used for the attachment of the carbonyls The active surface groups such as silanol and siloxane bridges react readily with the carbonyls, immobilizing them through direct surface bonding [32]

The rigid structure of the inorganic support can prevent the dimerisation The dimerisation deactivates the catalyst in the homogeneous system The metal complexes containing anchoring ligands prepared in homogeneous medium may be supported on an inorganic support under mild conditions A potential application of the inorganic supported complexes could be in the area of the bifunctional catalysts where one of the functions of the catalyst is associated with intrinsic properties of the support [33].

Other materials used as supports include magnesium oxide and carbon in the form of charcoal or carbon black. In recent times, zeolites with controlled pore size have gained a lot of importance as inorganic support [34]. Zeolites are water-containing crystalline aluminosilicates of natural or synthetic origin with highly ordered structures. They consist of SiO_4 and AlO_4^- tetrahedra, which are interlinked through common oxygen atoms to give a three-dimensional network through which long channels run.

In the interior of these channels, which are characteristic of zeolites, are water molecules and mobile alkali metal ions, which can be exchanged with other cations. These compensate for the excess negative charge in the anionic framework resulting from the aluminum content. The interior of the pore system, with its atomic-scale dimensions, is the catalytically active surface of the zeolites The inner pore structure depends on the composition, the zeolite type and the cations. The general formula of zeolites is

$$M^{I}M^{II}_{0,5}\,[(AlO_2)_x\ \ (SiO_2)_y\,.\,(H_2O)_z]$$

where M^{I} and M^{II} are preferentially alkali and alkaline earth metals

x and y denote the oxide variables

z is the number of water molecules

The experience in the use of zeolites based catalysts in the petrochemical industry can be applied to 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. An excellent example of alkylation is the Mobil-Badger process, which uses ZSM-5 type zeolite to produce ethylbenzene by alkylation of benzene with ethylene [34,35]. In this application, ZSM-5 acts as a strong solid acid and may be viewed as H^+ supported on the surface of the crystalline zeolite structure. The older, Friedel-Crafts aluminum chloride catalyzed process produces more by-products and suffers from the corrosivity of the catalyst system Another good example of this fact is the vapour phase Beckman rearrangement in the synthesis of caprolactum 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 unacceptable material as a by-product A number of studies have been reported on the catalysis with complexes attached to the inorganic support complexes and many large scale industrial processes are catalyzed by using such materials A summary of selected studies of metal complexes immobilized on inorganic supports is given in **Table 1.5.**

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 Recently aerogels offer interesting opportunities for catalysis due to their unique morphological and chemical properties

1.2.2 ORGANIC POLYMERS AS SUPPORT

Polymers as supports play a variety of roles depending on the system In some cases, polymer supports act only as carrier for the appropriate catalyst dispersed on the surface. In the other cases, the macromoleculer 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 the natural systems In all cases, 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 the 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 polymers vary widely depending on molecular weight, the chemical nature of the monomer or combinations of monomers and the conditions of polymerization which affect the arrangement of the polymer molecules and the interactions with one another Organic polymers normally used as supports are polystyrene, polypropylene, polyacrylates, polyvinylpyridine, polyvinylalcohol and polyvinylchloride **(Table 1.4).** Three major types of polymers are known [41-43]

1.2.2.1 GELLULAR OR MICROPOROUS POLYMERS

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

1.2.2.2 MACRORETICULAR OR MACROPOROUS POLYMERS

The polymers have a carefully controlled regular crosslinking (reticular) which allows a high internal surface area to the polymer [44,45] These are made either from styrene using divinylbenzene as the copolymer or from acrylates wherein donor ligand can be supported within as well as on the surface of the polymer

1.2.2.3 PROLIFEROUS OR POPCORN POLYMERS

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

Anchoring of multidendate ligands to insoluble polymeric supports is a technique now commonly utilized based on the pioneering efforts of Merrifield in polypeptide synthesis [43] 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 Poly(styrene-divinylbenzene) is the most widely used organic polymer as it can be functionalised easily with a wide range of physical properties with the result that its porosity, surface area and solution characteristics can be altered by varying the degree of crosslinking [46,47] 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 the polymer matrix as the polymer support stabilizes the unstable structure on the

surface For example, the catalytic solution of Wilkinson complex $RhCl(PPh_3)_3$ loses its activity on exposure to air but when the complex is supported on a polystyrene resin, it can be employed in the presence of air without deactivation [48]

2. Dimerization of the catalyst in the reaction mixture is 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 in order 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 ``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 into 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 size 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 mixture, the rate of hydrogenation for cyclohexene increased by a factor of 2 4 Hence, the choice of better swelling agent help to promote activity [49].

6. The degree of crosslinking affect the nature of the catalyst Polymer with varying degrees of crosslinking from 1% to 20% have been used as supports in the preparation of the catalysts The increased rigidity can 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 upon reduction gives catalysts active for the hydrogenation of alkenes, alkynes but the active species readily polymerizes leading to 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 [50]

In spite of the 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 sulphonated crosslinked polystyrene [51] The reasons for this situation are . **(a)** limited chemical stability especially above 100^0 C **(b)** poor mechanical properties **(c)** the reaction which are often typical to heterogeneous catalysis are diffusion limited since the active sites are buried inside the crosslinked support and **(d)** the supported catalysts can lose their activity on leaching of metal from metal complex anchored onto the support Recently, polymers having good mechanical strength with different degree of crosslinking have been used widely as supports [52-55]

Catalysis by ion exchange resins represents perhaps one of the earliest examples for the use of a polymer supported species [56]. Polymer supported phase transfer catalysts have been widely used in the organic synthesis to minimize the loss of the catalyst Surface enriched polymer supported phase transfer catalysis using vinyl toluene as a functional monomer was prepared and was found to be effective in dichlorocarbene addition to cyclohexene [57] A relatively new area of application in which polymer matrices are utilized on industrial scale as supports for enzymes in biocatalysed processes such as the synthesis of aspartic acid and fumaric acid of lactose free milk, 6- aminopenicillanic acid and conversion of acrylamide is rapidly expanding [58] Some of the reactions catalyzed by polymer supported transition metal complexes are listed in the **Table 1.6.**

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 macromoleculer support that acts as a asymmetric reagent or a catalyst in synthesis [67,68]. Recently, linear polytartarate ester supported $Ti(O\text{-}iPr)_4$ [tetraisopropoxy titanium (IV)] have been used as catalysts for asymmetric synthesis of epoxide from *trans*-hex-2-ene-1-ol with ee upto 80% conversion [69] Moreover, polycarbonate-$Fe(CO)_5$, polymethyl methacrylate- $Fe(CO)_5$, polyvinylidine fluoride-$Fe(CO)_5$ in DMF composites have been prepared and found to have magnetic recording applications [70] 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

It is noteworthy that the Royal Swedish Academy of Science awarded the **Nobel Prize in Chemistry for 2001 for the development of catalytic asymmetric synthesis.** One half of the award has been bestowed jointly on **William S. Knowles, St Louis, Missouri, US, and Ryoji Noyori, Nagoya University, Chikusa, Nagoya, Japan,** for their work on chirally catalyzed hydrogenation reactions The other half has been given to **Barry Sharpless, Scripps Research Institute, La Jolla, California** for his work on chirally catalyzed oxidation reactions

Table 1.4
Classes of supports

INORGANIC	ORGANIC
Silica	Polystyrene
Zeolites	Polyvinylpyridine
Clay	Polyvinylalcohol
Metal oxides	Polyaminoacids

Table 1.5
Metal complexes immobilized on inorganic supports

REACTION	METAL COMPLEX/SUPPORT	REF.
Olefin Metathesis	$Mo(CO)_6/Al_2O_3$	[37]
Benzene Hydrogenation	$Ni(CO)_4$/MX Zeolite	[38]
CO Reduction	$Fe_3(CO)_{12}/SiO_2$	[39]
Olefin Oligomerization	$Ni(CO)_4/\ \gamma\text{-}Al_2O_3$	[30]
Catalytic Reforming	$Re_2(CO)_{10}/Al_2O_3$ (Impregnated with Pt)	[40]

Table 1.6
Metal complexes immobilized on organic supports

REACTION	METAL COMPLEX	POLYMER	SUBSTRATE	REF.
Hydrogenation	$RhCl(PPh_3)_3$	Phosphinated 2 % poly (S -DVB)	Cyclohexene	[48]
	K_2PdCl_4	Amberlyst A 27	Styrene	[59]
Hydroformylation	$Rh(acac)(CO)_2$	Phosphinated amberlyst XAD-2	Hex-1-ene	[60]
Hydrosilyation	$Pd(PhCN)_2Cl_2$	Amberlyst A21 with Me_3SiOH	Butadiene	[61]
Oxidation	$FeCl_2.4H_2O$	Poly (4-vinylpyridine)	Cyclohexane	[62]
	$MoO_2(acac)_2$	Poly(benzimidazole)	Cyclohexene	[63]
	Mn(Salen)	Janda Jel	cis-β-Methyl-styrene	[64]
	Mn(salen)Cl	poly(methyl methacrylate)	1-Phenylcyclo-hexene	[65]
Isomerisation	Co(II)porphy-rin	polystyrene	Quadricyclane	[66]
Polymerization	$Co(acac)_2$	Polyvinylimidazole	butadiene	[57]

Many molecules appear in two chiral forms that mirror each other In nature one form 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- as was the case, 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

1.3 LITERATURE SURVEY ON POLYSTYRENE SUPPORTED CATALYSTS

Polymer-anchored transition metal complex catalysts have been investigated from two points of view One is based on polymer chemistry, and the other on catalysis chemistry From the viewpoint of polymer chemistry, a polymer - anchored transition metal complex catalyst is basically a functional polymer Its catalytic function originates from its transition metal complex component, while the polymeric component assists the complex in its work as an active and selective catalyst [22,23,72-79]

Polymer supported metal complexes are used as mechanochemical systems and as models of bioorganic systems The design and development of ion selective polymer supported reagents is an important application in environmental remediation, the removal of toxic metals from the industrial process streams and recovery of precious metals from low grade ores [80-82]. A number of industrial processes in which ion-exchange resins are based on sulfonated polystyrene The examples are the synthesis of methyl t-butyl-ether(MTBE), t-amyl methyl ether(TAME), bisphenol A, methylvinylketone, isoamylene and phenol alkylation [78]. Few examples of the typical polystyrene supported transition metal complexes used in specific reactions are listed in **Table 1.7.**

In the 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 complex from the polymer matrix, when monodentate or non chelated ligands are used could be overcome by use of bidentate or chelating ligands, having nitrogen or oxygen as donor atoms giving a co-ordinatively stable catalyst with higher activity

The polymeric supports that have been most commonly used are croslinked 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 easily functionalised 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 phenyl ring The chloromethylated styrene-DVB copolymer referred to as Merrifield's resin and designated as Ⓟ—CH_2Cl is the most important intermediate for the synthesis of functionalized polymer A survey of main functional groups that can be prepared starting with Ⓟ—CH_2Cl is given in **Scheme 3**

A variety of ligands such as porphyrin derivatives, macrocyclic pyridylamines and Schiff bases have been employed [90,91] Schiff bases are one of the most versatile and thoroughly studied ligands but very few reports are available of polymer anchored Schiff base and their application in catalysis [28,29,92-94] Schiff base complexed with transition metal are used as catalysts in the selective epoxidation of olefins Almost all these catalysts require a mono oxygen source such as hydrogen peroxide, tert-butylhydroperoxide, iodosylbenzene, cumene hydroperoxide etc., to carry out oxygen transfer to the olefins Ram and Co-workers [95,96] synthesized poly(styrene divinylbenzene)Pd(II) and Rh(III) complex using 1,2-diaminopropane, trimethyldiamine, glycine, L-2 aminobutanol (L-2 AB), ethylene diamine- tetraacetic acid (EDTA) and found them to be effective catalysts in the hydrogenation and oxidation of olefins and nitroaromatic compounds under mild reaction conditions.

3 1 AIM AND OBJECTIVE OF THE PRESENT WORK

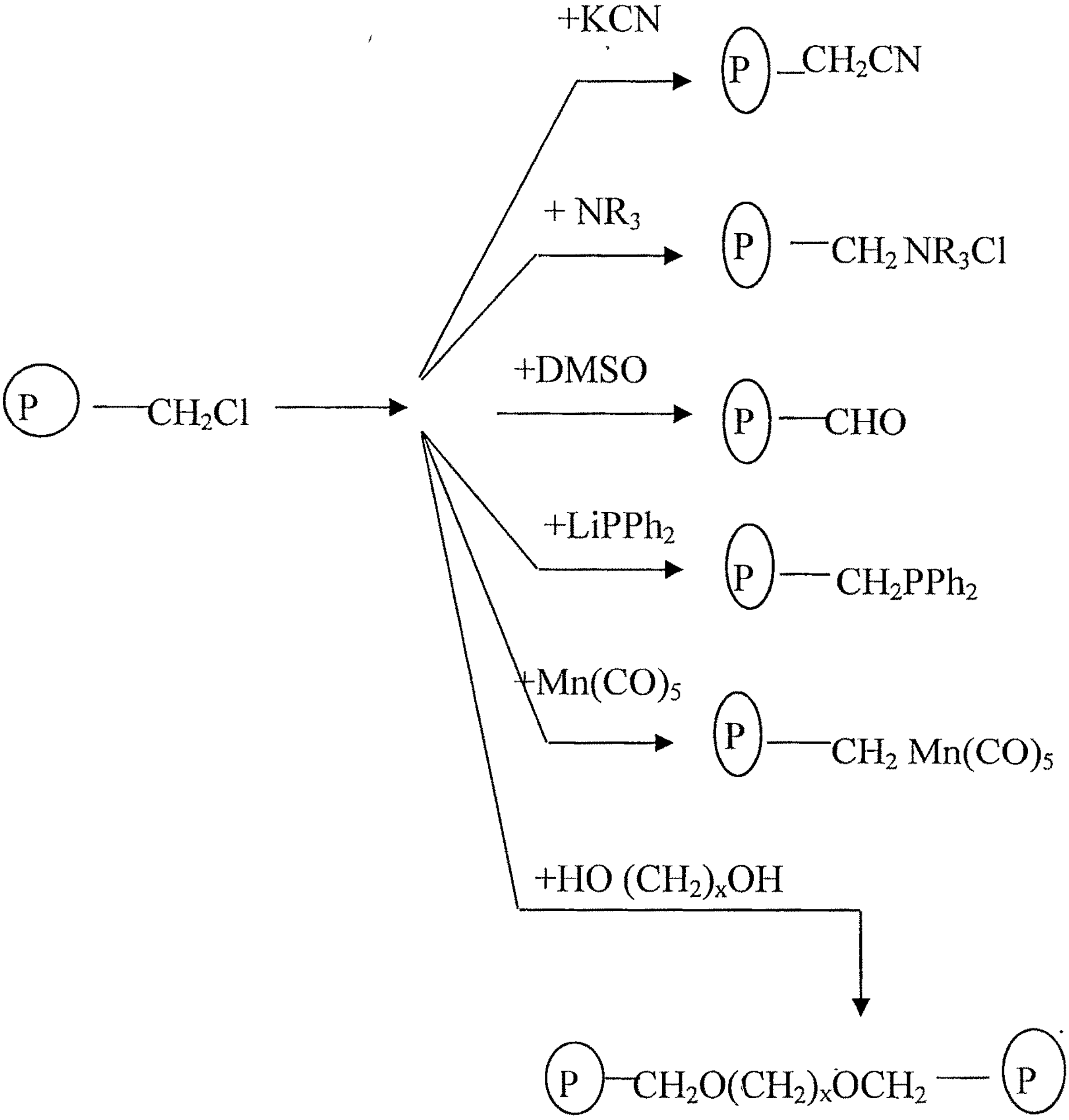
The main objective of the present work is to heterogenize the homogeneous transition metal complex catalysts To synthesize a Schiff base liganded and bidentate, five coordinate chelates functionalised polymer by condensation of aldehydes with polymer-attached diamines and use these functionalized polymers to synthesize polymer supported metal complex by complexing with the metal salts and evaluate their catalytic activity in the epoxidation and hydrogenation of olefins. The polymer used was the commercially available poly (styrene-divinyl benzene) with different degree of crosslinking. The Schiff bases obtained by the anchoring 1,3-diamino propane and 4,4'-diamine biphenyl with polymer and subsequent condensation of the polymer attached diamines with salicylaldehyde. The polymer supported metal complexes were synthesized by complexation of the functionalized polymer with Ru(III) and Mn(II). Their catalytic activity was investigated in the model reaction· viz epoxidation of *cis*-cyclooctene and norbornene and Pd(II) catalysts in the hydrogenation of 1-decene

In short the present study includes .

1. Synthesis of polymer anchored Ru(III), Mn(II) and Pd(II) complexes. The Schiff base complexes are synthesized using chloromethylated styrene - divinyl benzene copolymer with 5% and 8% crosslinking followed by sequential attachment of 1,3-diaminopropane, 4,4'-diaminobiphenyl and salicylaldehyde and finally, treating with an ethanolic solution of $RuCl_3$, $MnCl_2$ or $PdCl_2$

Table 1.7
Reactions carried out using polystyrene supported transition metal complexes

REACTION	SUBSTRATE	CATALYST	REF.
Hydrogenation	Cycloocta 1,3-diene	Chloromethylated crosslinked polystyrene supported titanocene	[83]
	Cyclohexene	8% crosslinked polystyrene supported [Rh$(CO)_2$ pentane-2,4-dione]	[84]
	Nitrobenzene	Chloromethylated 8 % poly(styrene divinyl benzene) supported Pd(II) L-2 aminobutanol	[85]
Olefin metathesis	*cis*-2-Pentene	Poly(styrene-divinyl benzene) supported $Cl_2(PR_3)_2Ru=CH-CH=CPH_2$	[86]
Oxidation	*cis*-Cyclooctene and/styrene	Chloromethylated 8 % and 14 % poly(styrene divinyl benzene) supported Ru(III)	[28]
	Styrene, Cyclopentene Cyclohexene	Poly(styrene divinyl benzene) supported Fe(II), Co(II), Ni(II), Cu(II)	[97]
	Cyclohexene	Polystyrene supported Phosphotungstic complex	[87]
	Cyclohexene	Polystyrene supported 2,2'-bipyridine $NiCl_2$ complex	[88]
	Cyclohexene	Polystyrene supported $MoO_2(acac)_2$ and $VO(acac)_2$	[89]
	cis-β-Methyl-styrene	Polystyrene supported Mn(Salen) complex	[64]



Scheme 3 : **Functionalized polymeric supports**

2. Characterization of the newly synthesized complexes by physicochemical methods such as surface area, pore volume, apparent bulk density, moisture content, swelling behaviour, chemical analysis, infra-red, UV-VIS reflectance, thermogravimetric analysis, morphological studies of the complexes reinforced by Scanning Electron Microscopy and by ESR An attempt was made to propose the probable structure of the catalysts on the basis of spectroscopic techniques

3. Investigation of the complexes as catalysts for the model reactions

   (i) Epoxidation of *cis* - cyclooctene and norbornene using t-butyl hydroperoxide (TBHP) as an oxidant using Ru(III) and Mn(II) complex catalysts ·

   (ii) Hydrogenation of 1 - decene using Pd(II) complexes catalysts

4. Life cycle studies of the catalysts

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

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