CHAPTER # 1

INTRODUCTION

1.1 INTRODUCTION

Catalysis played an important role in establishing the economic strength of the chemical industry in the first half of the 20th century and the clean technology revolution in the industry will provide newer opportunities for catalysis and catalytic processes (1). Some of the major goals of the clean technology in chemical industries are to increase process selectivity, to maximise the use of starting materials and to facilitate easy separation of the final reaction mixture including the efficient recovery of the catalyst. Other important factors such as regenerability and cost of the catalysts should also be included.

The catalysts have normally been classified into two broad categories i.e. (i) homogeneous and (ii) heterogeneous.

The activity and selectivity of the homogeneous catalysts are found to be higher because of their better defined catalytic sites under mild operating conditions. Theoretically all the atoms or molecules of the catalysts are available to the reactants. After chemical modification, it controls the electronic and steric properties of the metal centres. Their activity and selectivity may be tailored by varying the ligands attached to the metal atom. The reaction mechanism can be explained easily in case of homogeneous catalysts (2).

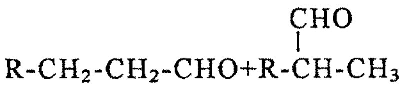
The major disadvantages of these types of the catalysts are however, problem of the recovery of the catalysts from the reaction system, the cost of the precious metals as well as the problem of suitable solvent where the whole system is present in homogeneous medium. It can be deactivated readily by various reactions which produce inactive species. Thus, a decrease in catalytic activity was observed in Wilkinson's catalyst $RhCl(PPh_3)_3$ when exposed to air (3,4). The dimerization of the catalysts at higher concentration could be responsible to diminish the catalytic activity. Therefore, homogeneous catalysts have often been found to have limited commercial utility on a large scale (5). Few examples where homogeneous catalysts have been used commercially are shown in Table 1.1.

On one hand homogeneous catalysts gained a new momentum and research has been directed throughout towards heterogeneous system. Though these catalysts are frequently less active and selective, they are very durable and could be separated easily from the reaction system. They may be used in fixed beds in gas-solid and liquid-solid contact reactors. Due to their higher thermal stability, heterogeneous catalysts can be used at higher temperatures.

The major disadvantages of the heterogeneous catalysts are however that (i) They have poorly defined sites (ii) limited accessibility and effectiveness of the catalytic components (iii) severe and costly reaction conditions and (iv) poor selectivity.

It would therefore be ideal to combine the advantages and simultaneously to avoid the disadvantages of each class of the catalysts by attaching homogeneous catalysts to a solid support in such a way that the ligand sphere of the metal is essentially unchanged. This class of the catalyst sometimes referred to as "heterogenised homogeneous catalyst" could function mechanistically as if it in solution but it would operate as a

TABLE 1.1 Industrial Processes involving Homogeneous Catalysts

Process	Reaction	Typical catalyst	Temp. (°C)	Pressure (atm.)
Wacker	$C_2H_4+\frac{1}{2}O_2 \longrightarrow CH_3CHO$	$PdCl_2$ / $CuCl_2$ (aq)	110	5
Vinyl acetate	$C_2H_4+\frac{1}{2}O_2 + CH_3COOH$ $\longrightarrow CH_3CO_2\text{-}CH{=}CH_2+H_20$	$PdCl_2$ / $CuCl_2$ (aq)	130	30
		$HCo(CO)_4$ in org. solvent	150	250
OXO	$R\text{-}CH{=}CH_2+CO+H_2 \longrightarrow$	OR		
	 $R\text{-}CH_2\text{-}CH_2\text{-}CHO+R\text{-}\overset{\overset{CHO}{\vert}}{C}H\text{-}CH_3$	$RhCl(CO)(PPh_3)_2$ in organic solvent	100	15
Methanol Carbonylation	$CH_3OH + CO \longrightarrow CH_3COOH$	$RhCl(CO)(PPh_3)_2$ with CH_3I promoter in organic or aqueous solution.	175	15
Ziegler -Natta	$C_2H_4 \longrightarrow 1/n\ (C_2H_4)n$	α $TiCl_3(S) + Al(C_2H_5)_2Cl$	70	5
Polymerization	$C_3H_6 \longrightarrow 1/n\ (C_3H_6)n$	Suspended in organic liquid	100	10

separate immobile phase. The major advantage of this type of the catalyst is the separation from the reacting system and its reuse. Thus, this new class of the catalyst has been subject of extensive research. These catalysts are also called supported or anchored catalysts.

1.2 HETEROGENISED HOMOGENEOUS CATALYSTS

The soluble metal complexes that are active homogeneous catalysts have a metal centre which functions as an active site for catalysis. The metal centre of a homogeneous catalyst bound to the coordinating ligand is responsible for the higher catalytic activity. These homogeneous catalysts could be heterogenised on the surface of the solid by different approaches.

The main approach to heterogenise the homogeneous catalyst is the incorporation of ligand forming functionalities on to a polymeric structure and then forming the ligand metal complexes by a route analogous to that is used to prepare homogeneous complexes. This class of the catalyst known as the polymer anchored catalyst is an interesting and relatively newer area of the research (6-11).

The term " heterogenised homogeneous " is defined as the process whereby a transition metal complex is immobilised on an inert polymer or inorganic support through covalent linkage. It is a new development of the catalyst and a boundary between the homogeneous and heterogeneous system. This type of research provides the preparation of new class of the catalysts. The major advantages of the supported metal complex catalysts are :

(1) The catalyst can be separated easily from the reacting system and can be reused.

(2) 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 a commercial scale.

(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) The use of a wide range of solvents for a homogeneous catalyst is often limited by solubility characteristics of the catalyst; this clearly presents no problem for a polymer supported catalyst.

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

(6) It is generally agreed that homogeneous catalysts invariably involve atleast one intermediate in which the metal atom is " co-ordinatively unsaturated ". Such an unsaturated intermediate exhibits a tendency very often to dimerize in order to gain better stability, which is detrimental to the catalytic activity. Polymer supported catalysts are rigid enough to prevent the interaction of such isolated coordinatively unsaturated metal atoms thereby preserving all of the potential activity.

(7) In addition to the normal selectivity observed in homogeneous catalysis, with polymer supported catalysts the polymer support itself can induced changes in the catalyst's selectivity in many instances (12).

(8) Attachment of a metal complex to support can sometimes provide some protection for the catalytic species against poison.

Hence, it is obvious that the supported or heterogenised homogeneous catalysts will be of a new class of the catalyst known as the hybrid catalyst and possess the advantages of both homogeneous and heterogeneous catalysts.

In order to synthesise the heterogenised homogeneous catalysts, the following points are to be considered.

(i) The surface area of the support to which the metal complex is to be attached.
(ii) The capacity of the specific support to attach the ligand functionality itself to the surface under specific reaction conditions to which the metal complex is to be exposed during application as a heterogeneous catalyst.
(iii) The stability of the support under catalyst reaction condition or during any catalyst regeneration step.
(iv) The stability of the anchored metal complex itself on a particular support under the reaction condition.
(v) The steric requirements of the metal complex on the surface of the support.

The support to which the metal complex is to be attached should be stable at the temperature and pressure required for the reacting system under consideration. It is, therefore, important to use ligands which after coordinating strongly give thermally stable complex (12,13). An inert complex was found to be more stable than a labile complex. Mostly chelated complexes were found to be inert and less labile than non chelated ones (14).

The more stable chelated metal complexes can be obtained by the use of tri or tetradentate ligands however this may impart such rigidity to the polymer catalyst combination that catalytic ability may be lost (15).

1.3 TYPES OF THE SUPPORTS

Mainly two broad types of supports have been used to synthesise the supported metal complex catalysts (i) Inorganic oxides and (ii) Organic polymers.

1.3.1 INORGANIC OXIDES AS SUPPORT

The major advantages of inorganic supports over their organic counterparts are their better mechanical and thermal stabilities coupled with resonable heat transfer stability. Very often the upper limit of the thermal stability of organic polymer supported complex catalyst is set by the polymer rather than the metal complex (16).

Inorganic oxides and glasses have been employed widely in large scale applications, perticularly in plants operating high temperature catalytic processes. However, attempts have also been made to reproduce the elegant synthesis of structurally well defined polymer supported reagents employing various inorganic supports. The supports that have been widely used include silica, alumina, glasses, clays and zeolites (17)

The rigidity of the inorganic supports can prevent the dimerization which deactivates the catalyst in the homogeneous system. Well characterized metal complexes containing anchored ligands prepared in homogeneous medium may be supported onto an inorganic support under mild condition. A potential application of the inorganic supported complexes could be in the area of bifunctional catalysts where one of the functions of the catalyst is associated with the instrinsic properties of the support (18). Inorganic supports can be selected for stable diffusional characteristics at the most reaction conditions (19). Zeolites were found to be a very good inorganic support because of their well defined controlled pore size (20-23).

The main disadvantage of the supported catalyst using inorganic oxides as support is the leaching of the metal complex catalyst from the support to the solution. It has a lower number of active sites per unit weight than the more highly substituted polymers.

1.3.2 ORGANIC POLYMERS AS SUPPORT

There are mainly three types of the polymers which have been used as supports (i) microporous polymers (ii) macroreticular or macroporous polymers and (iii) popcorn polymers.

Microporous polymer is a simple type of polymer in which the long strands of polymer molecules are either crosslinked or merely entangled randomly. Macroporous polymers have a carefully controlled regular cross-linking which allows a high internal surface area to the polymer (24,25). Popcorn polymers are formed spontaneously in butadiene and butadiene copolymer. They are hard, porous and opeque materials (26,27).

Organic polymers normally used as supports are polystyrene, polypropylene, polyacrylates and polyvinyl chloride. Polymers offer many advantages over other supports (28).

Polymers, especially poly (styrene - divinyl benzene) can be synthesised with a wide range of physical properties and it can be functionalised easily. As a result their porosity, surface area and solution characteristics can be altered by varying the degree of crosslinking (29,30). Unlike metal oxide surfaces, most hydrocarbon polymers are chemically inert and hence do not interfere with the catalytic group.

The other important attractive feature of organic support is the opportunity they offer to introduce extra selectivity into the catalyst through the control of diffusion of reactants with the polymer. The common methods used to reduce the diffusion limitation of anchored catalysts are to decrease the particle size, to increase the overall surface area of the catalyst and to introduce a bimodal pore size distribution allowing rapid diffusion through a portion of the catalyst. The catalytic activity of polymer supported catalysts was found to be higher sometimes than the inorganic oxide used as a support (31). Thus dechlorination of chlorobenzene by hydrogen molecule has been carried out in the presence of both a polymer supported and alumina supported p-phenylene phthalamide H_2PtCl_2 complex and a higher activity was observed with the former one.

However the major disadvantage of the polymer as the support is the difficulty in analysing the residues attached to the polymeric material. This is because of the insoluble nature of the support which makes it difficult to be analyzed by conventional techniques. Only a small portion of the active component is accessible and effective and the control that can be exerted over the composition and structure of the active sites is relatively limited. The overall chemical, mechanical and thermal stability of the support can be limited which prevent the catalyst from being used in stirred reactions in which they are pulverised. Recently polymers having good mechanical strength with different degree of crosslinking have been used widely as supports (32-35).

Catalysis by ion exchange resins represents perhaps one of the earliest examples for the use of a polymer supported species (36). The conventional anion exchange resins have been employed as supported phase transfer catalysts (37) and a number of new supported analogues of phosphonium salts have been prepared specifically with this catalytic function in mind. The major advantages in using ion exchange resins as catalysts is that they are readily available. A wide range of organic synthesis has been accomplished using the acidic and basic forms of ion exchange resins as catalyst (38). However the thermal stability of ion exchange resin restricts its use as a catalyst support for high temperature reactions (38). The use of inorganic oxides as catalyst and catalyst support offers a remedy for such problems. Among the studied inorganic oxides silica, alumina and zeolites have received a considerable attention due to their unique structural properties and high thermal stability (39). Thus kotasthane et al have synthesised a number of zeolite-based catalysts useful in petrochemical reactions. However, the use of inorganic oxides as a support for liquid phase catalysed reaction is found to be limited due to the leaching of catalyst species from its surface during the course of reaction. To overcome such barrier a concept of phase transfer and biphasic catalyst has been introduced (40). Both types of the catlysts can be viewed as an extension of homogeneous catalyst with an increased efficiency in terms of recycling process (41).

The catalytic activity of metal complexes in homogeneous medium has received much attention now a days due to their structural variety as well as catalytic role in various reactions such as hydrogenation (42-50), oxidation (51-56), epoxidation (57-60), polymerization (61-63), hydroformylation (64-66), carbonylation (67,68) and isomerization (69-71). Skoda folder and Kollar studied the hydrogenation of steroidal dehydroamino acid ester using soluble Rhodium phosphine complexes and it was found to be selective for 3,5 dienes (72). The hydrogenation of 1-hexene and benzene was carried out at 80°C and 6.5 atm of H_2 using Rh - complexes in homogeneous system (73) The kinetics of hydrogenation of acrylonitrile-butadiene copolymer was studied by Mohammadi and Rempel using Rh-complexes and various thermodynamic parameters were calculated (74). These metal complexes were found to be suitable for assymetric synthesis. Nagel (75) used the tartaric acid backbone to synthesise phosphine ligands such as Degphos, the rhodium complex of which was found to be highly efficient catalyst for the assymetric hydrogenation of prochiral substrates. These precious metal complex catalysts were observed to be having a dramatic impact on synthetic organic chemistry and chemical technology. Examples are palladium catalysed oxidation of ethylene to acetaldehyde (76), rhodium catalysed carbonylation of methanol to acetic acid (77) as well as hydroformylation of olefins (78,79) and hydrosilylation of olefins (80,81). palladium complexes have been used for arylation and vinylation of the olefins which provide a new method for the synthesis of organic compounds. Mukherjee et al (82) studied the reduction of aliphatic and aromatic nitro compounds using dinuclear orthometallated Ru(II) complexes and a probable reaction mechanism was suggested. These soluble metal complexes used as catalysts in biphasic media are gaining a considerable interest in recent years because of their practical advantage for the separation of the catalysts and the products(83). Purwanto and Delmas studied the hydroformylation of 1-Octene in two phase system using water soluble Rh - complexes and TPPTS (Tri sodium salt of tri (m-sulfophenyl) phosphine)as a water soluble ligand (83a).

Recently aerogels offer interesting opportunities for catalysis due to their unique morphological and chemical properties. These properties originate from their wet chemical preparation by the solution-sol-gel (SSG) method and their subsequent liberation from the solvent.. Pajonk reviewed aerogels in catalysis upto the year 1990, covering preparation, physicochemical properties and catalytic applications of mainly high-temperature aerogels. A pertinent survey of reaction classes updated to 1994, demostrates the wide range of both reactions and aerogel materials used as catalysts. These include the partial oxidation of acetaldehyde to acetic acid catalysed by SiO_2, Pt-SiO_2 etc., epoxidation of 1-hexene, cyclohexene to their corresponding epoxides (84) by TiO_2 - SiO_2, hydrogenation of benzene to cyclohexene catalysed by Rh on TiO_2 - SiO_2 (85), nitrobenzene to aniline catalysed by

Pd - Al_2O_3 (86) etc. But the aerogel -based catalysts or catalyst supports have so far found only limited application in catalytic processes, mainly due to their rather expensive method of preparation and the various difficulties encountered in operating reactors when using these materials.

Today enviornmental pollution has been identified as the primary cause of concern by WHO (87). The vehicle's emmission which constitute major part of toxic gases like NOX and CO, is one of the causes of enviormental pollution. Thus, attempts are being made to control their emmission. The catalysis science has shown the way for such control, where in the the oxidation of toxic gases is proposed. This has given rise for the birth of catalytic convertor is made up of a catalyst system which essentially contain transition metals anchored on a support of high surface area. Thus the catalyst system is basically oxidation type of the catalyst wherein supported metal species oxidises the toxic gases at high temperature (89).

1.4 AIM AND OBJECTIVE OF THE WORK

The present study is an attempt to have better understanding of polymer bound catalyst systems in hydrogenation and oxidation reactions through detailed experimentation. Equal emphasis has been placed on catalyst development, characterization and the activity of the catalysts. The work is oriented towards the specific reactions namely the hydrogenation of nitrobenzene and oxidation of toluene using ruthenium (III) and palladium (II) metal complexes supported onto different crosslinked styrene-divinyl benzene copolymer It has been reported that the polymer anchored non-chelated metal complexes are less stable and leach out into the solvent while chelated complexes are more stable and less labile than the nonchelated ones (14). In the present investigation, therefore, approach has been made to synthesise the metal complex catalysts in such a way that the transition metal ions are bound to a chelating ligand through sequential attachment on to the polymeric support.

The present study includes :

(i) Synthesis of polymer anchored metal complexes by sequential attachment of functional group, ligand and metal ions on polymeric support.
(ii) Synthesis of the metal complex similar to one attached to polymer support, for comparison of catalytic activity in homogeneous system.
(iii) Characterization of the synthesized catalysts using conventional as well as spectroscopic methods.
(iv) Investigation of the catalytic activity of the synthesized catalysts for the hydrogenation of nitrobenzene as well as the oxidation of toluene.
(v) Investigation of the influence of various parameters such as concentration of the catalyst and the substrate, nature of the solvent and temperature of the system.
(vi) The recycling efficiency of the fresh and the used catalysts.

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