CHAPTER 1
INTRODUCTION

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1.1 Introduction

Catalysts play an exceptionally important role in living nature. It is found that most reactions such as oxidation, reduction, hydrolysis, dehydration in living organisms occur at the required rate owing to the participation of biological catalysts. Metals are among the many catalysts which stimulate natural processes. Now, for known reactions suitable catalyst materials are known and are readily available in most instances. Primary factors which govern the choice of useful catalysts in a known process are activity, selectivity and physical suitability. Other important factors such as regenerability and cost of the catalysts are also included.

Catalysts have normally been classified into two broad categories viz.

i. Homogeneous and
ii. Hetergeneous

Homogeneous reactions take place under mild conditions with higher efficiency, selectivity and stereospecificity. The mechanism of the reaction is also simple when compared to heterogeneous catalysts (1). However, a major disadvantage of homogeneous catalyst is the recovery from the reacting system as well as it cannot be used at higher temperatures. This severly hampers the use of a homogeneous catalyst for industrial purposes.

On this background heterogeneous catalysts gained a new momentum and research has been turned to heterogeneous catalysts. The main advantages of heterogeneous catalysts are ready removal of catalyst together with their recovery and re-activation for reuse. They are active over a wide range of reaction conditions. Thermal stability and ease of handling in large scale operations also make heterogeneous catalyst a more useful one.

However, the main disadvantages of the heterogeneous catalysts are that of the less selectivity and atoms in a particular site on a metal surface provide active sites. These catalysts also require elevated temperatures and vigorous reaction conditions.

It would be ideal to combine the advantages and avoid the disadvantages of both homogeneous and heterogeneous catalysts. Efforts have been made to design a catalyst so as to have advantages of the above mentioned catalysts, known as heterogenised homogeneous catalysts. In this, a metal ion is anchored on to a solid support through a suitable ligand.

The solid supports may be either inorganic oxides or a rigid organic polymer. Thus a new field of catalysis has been developed and is known as supported or anchored catalysts. Now-a-days a variety of supported catalysts are available which can meet the necessary requirements to be used for industrial purposes.

The main reasons(2) for supporting metal complexes are:

i. 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.

ii. Organic functional groups covalently bound to the surface of crystalline solids e.g. polymers are subject to special constraints which may alter their chemical reactivity relative to the analogous small molecules.

iii. supporting a metal complex with the help of a multidentate ligand may alter the stereochemistry around the metal ion in a beneficial way.

iv. Supporting a metal complex may alter the position of equilibrium between metal ions and their surrounding ligands.

v. By supporting a complex it is sometimes possible to stablize catalytically active but normally unstable structures.

vi. Attachment of a metal complex to a support can sometimes provide some protection for the catalytic species against poison such as water or atmospheric oxygen.

Hence it is obvious that the supported or heterogenised homogeneous catalysts will be a new generation of catalysts and they possess the advantages of both homogeneous and heterogeneous catalysts.

1.2 Heterogenized homogeneous catalysts :

The catalytic properties of most of the compounds are dependent on their ions and their immediate surroundings. It would therefore be ideal to combine advantages and simultaneously minimize the disadvantages of homogeneous and heterogeneous catalysts. This could be achieved if homogeneous catalysts are either deposited into a solid support or better chemically bound to it in such a way that the attached complex bathed by the solvent and reactants in the reaction mixture. This class of the catalyst is called heterogenized homogeneous catalysts. (2-7)

The term heterogenized homogeneous is defined as the process whereby a transition metal is anchored to an inert polymer or organic support through covalent linkage. The major advantages of supported metal complex catalysts are the easy seperation from the reactants and products, specificity, controllability and reproducibility.

A number of methods have been adopted in order to anchor the homogeneous catalyst. The common method is to attach the metal ion to a solid support by adsorption or by an ionic or covalent chemical bond. Another way is polymerizing the catalyst to such a high molecular weight that it becomes insoluble in the medium in which it is to be used, or by trapping it in a gel or other porous medium. Still another approach to heterogenize homogeneous catalysts is the incorporation of ligand forming functionalities into a polymeric structure and then forming the ligand-metal complexes by a route analogous to that and to prepare homogeneous complex. This class of anchored catalysts is referred to as polymer-anchored catalysts.

In order to synthesize the heterogenised homogeneous cataysts, the following points are to be considered.

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 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.

The support and the catalyst both should be stable at the temperature and pressure required for the reaction under consideration. Hence the ligand may be chosen in such a way which after co-ordination give thermally stable complexes (8-9). Chelated complexes are inert and less labile than non chelated ones (10,11).

Two broad classes of supported complex catalysts have been developed. In the first class, the metal complex is linked to the support through attachment to one of its ligands and the environment of the metal ion is unaltered on supporting. In the second case, reaction of a metal complex with the support results in displacement of ligands attached to the metal and their substitution by groups that form an essential part of the support.

1.3 Types of supports :

Mainly two types of the materials have been utilized as the support viz inorganic oxides and organic polymers.

1.3.1 Inorganic supports :

Inorganic supports that have been used include silica alumina, glasses, clays and zeolites (13). The advantages of inorganic supports over their organic counterparts are their better mechanical and thermal stabilities coupled with reasonable heat transfer properties. Generally the upper limit of the thermal stability of organic polymer supported complex catalysts is set by the polymer rather than the metal complex (14).

The rigid structure of the inorganic support can prevent the dimerization which deactivates the catalyst in the homogeneous system. Well characterized 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 bifunctional catalysts where one of the functions of the catalyst is associated with intrinsic properties of the support (15). Zeolites with their well understood controlled pore size are good inorganic supports (16-19). However, the main disadvantages of inorganic anchored catalyst is the leaching of the catalyst from the support to the solution. It has a lower number of catalytic sites per unit weight than the more highly substituted polymers.

1.3.2 **Organic polymer as support**

Organic polymers that have been used as supports include polystyrene, polypropylene, polyacrylates and polyvinyl chloride. They offer several advantages over other supports (20).

i. They are easily functionalized.
ii. Unlike metal oxide surfaces, most hydrocarbon polymers are chemically inert. As a result the support does not interfere with the catalytic group.
iii. Polymers can be prepared with a wide range of physical properties.

Poly (styrene divinylbenzene) can be prepared with a wide range of physical properties. As a result their porosity, surface area and solution characteristics can be altered by varying the degree of cross linking. (21-22) Due to their inert nature it does not interfere with the catalytic group.

One of the highly attractive features of organic polymer supports is the opportunity they offer to introduce extra selectivity into the catalyst through the control of diffusion of reactants within the polymer. However, their poor heat transfer ability and their poor mechanical properties prevent them from being used at high temperatures and in stirred reactions in which they are pulverized. Now-a-days polymers having good mechanical strength have been studied widely (23-26). A number of polymer supports are commercially available which possess high mechanical strength and with different degree of cross linking.

The catalytic activity of platinum group metal complexes in solution were reported in a number of reactions including homogeneous hydrogenation (27-30). These metal complexes have received much attention in recent years because of the structural variety and their role in catalytic reactions such as hydrogenation (31-35), oxidation (36-40), epoxidation (41-44), hydroformylation (45,46) carbonylation (47,48), metathesis (49-51), polymerization (52-54) and isomerization (55-57) of olefins. These complexes were also used in asymmetric synthesis (58), oxidative addition (59) and activation of small molecules such as O_2 (60), N_2 (61-62), H_2(63), CO(64) and NO(65) within the co-ordination sphere of the metal ion.

Recently these metal complex catalysts have been used as phase transfer as well as asymmetric catalysts. Polymer supported chiral Rhodium (I) complexes have been used for asymmetric hydrogenation of olefins by Kagan et al. (66). Oxidation of benzyl alcohol to benzaldehyde has been carried out by polymer supported phase transfer catalyst (67). Rh(I) complexes supported on polystyrene has been used for the asymmetric hydroformylation of olefins (68). Pd (II) and Rh (I) supported on polymer have been used in order to study the selective hydrogenation and enantioselective hydrosilylation (69-70) of cyclooctadiene and acetophenone.

Ruthenium (III) complexes in homogeneous system have been widely used as catalysts for various reactions mainly due to their high catalytic activity under mild operating conditions (71-73). However there are not many reports for hydrogenation and oxidation reactions using supported systems. Much of the research in this field is patended (74-76). The first published work on supported metal complex catalysts involved the use of cationic $[Pd(NH_3)_4]^{2+}$ and $[Pt(NH_3)_4]^{2+}$ supported on sulphonated polystyrene, used for olefin hydrogenation (77-78). Sivasankar et. al (79) studied the oxidation of cyclohexane using titanium silicate molecular sieve. Iron, Ruthenium and Copper supported on polymers have been used to study the oxidation of cyclohexane (80-81).

1.4 Aim and Objective of the work :

The main objective of the present work is to heterogenise the homogeneous transition metal complex catalysts and to investigate their catalytic activity for industrially important reactions. The work is more oriented towards the hydrogenation and oxidation of cyclohexene and cyclohexane respectively using Palladium (II) and Ruthenium (III) complexes of 1,2-diaminopropane anchored on to various crosslinked styrene divinylbenzene copolymer. Many polymer bound non-chelated complexes are reported to be less stable and leach out into the solvent under the reaction conditions. Chelated complexes are more stable and less labile than non-chelated ones. The present investigation is therefore taken to synthesize the catalysts in such a way that the transition metal ions are bound to a chelated ligand through sequential attachment onto the polymeric support. Such systems are expected to be more stable than the non chelated ones.

The present study includes :

1. Synthesis of macroporous polymer (Co-polymer of styrene and divnylbenzene) support with different degree of crosslinking.

2. Alternatively, use of commercially available copolymer (XAD-2 and XAD-8) as support.

3. Funtionalization of the copolymer by introducing chloromethyl group onto the polymer matrix, treatment with bidendate ligand and finally attachment of the metal ions to form the appropriate metal complexes on the polymeric support.

4. Synthesis of the chelated metal complex similar to the polymer anchored metal complexes to study the catalytic activity in a homogeneous system.

5. Characterization of the prepared catalysts using conventional and spectroscopic methods.

6. Investigation of the catalytic activity of the synthesized catalysts for the hydrogenation of cyclohexene as well as the oxidation of cyclohexane under various conditions.

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