Chapter - 1

INTRODUCTION

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1.1 Introduction

The research directed towards the design and the development of catalysts is an area of intense interest. Catalysis has been one of the most important challenges facing the practicing technologist in the development of new processes or practical reactions. Finding a good catalyst is especially difficult, since catalysis has been thought to be a vast and confusing field.

Catalysis provides an opportunity for technical exchange with many disciplines (1). Modern catalysts must rely on the integration of a broad range of technical expertise and experimental capabilities. It is therefore essential to have an understanding of the various disciplines such as chemistry and chemical engineering. A brief outline is given in Figure-1.1.

In a classical approach the catalysis has been classified into two broad categories i.e. heterogeneous and homogeneous; the former commonly is interpreted by the adsorption of the reactant and the product on the surface while the latter through the formation of an intermediate complex. A third type of the catalyst known as the supported catalyst has been developed which combines the advantages and minimizes the disadvantages of the homogeneous and heterogeneous catalysts. As shown in Scheme-1.1 metal ions, coordination complexes, metal clusters and enzymes constitute the bulk of homogeneous catalyst. Active metal complexes fixed on inorganic support or polymers via functionalization act as anchored catalysts. A variety of heterogeneous catalysts namely bulk

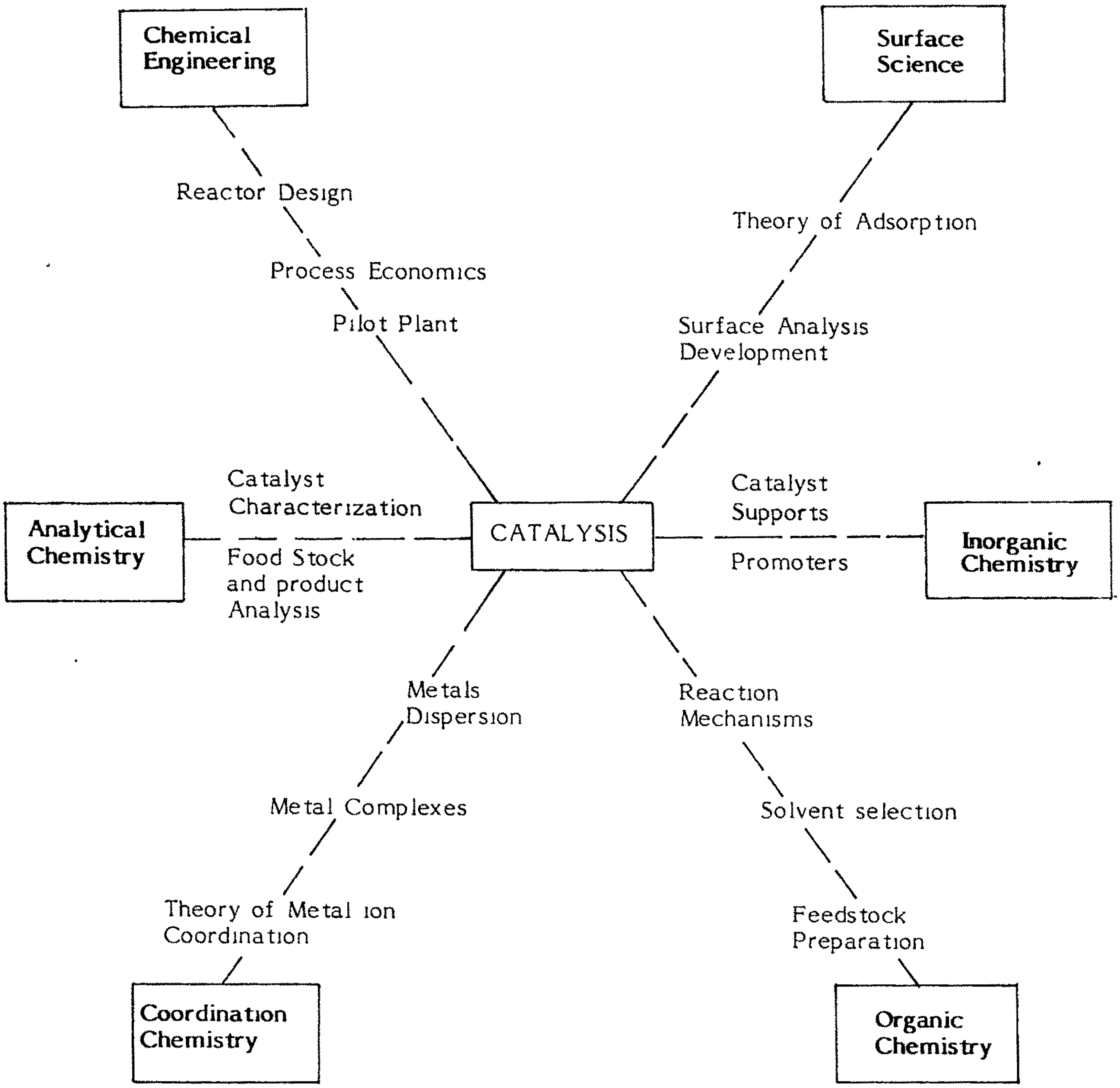

Figure-1.1 Technical dependence of catalysis metals, oxides, sulphides, alloys, mixed metal oxides and supported metal/metal oxides are widely used.

SCHEME-1.1

Catalysts

Homogeneous Catalysts

- Metal ions
- Coordination complexes
- Metal clusters
- Enzymes

Anchored Catalysts

- Polymer supported

  or

- Heterogenized homogeneous complexes

Heterogeneous Catalysts

- Bulk metals/ oxides
- Alloys, Mixed metal oxides
- Supported metals
- Supported oxides
- Zeolites

A comparison of the two types of the catalysts is given in Table-1.1. There are some obvious advantages of homogeneous catalysis (2). The reation takes place under mild conditions with higher efficiency, selectivity and stereospecificity. It is easy to study kinetics of the homogeneously catalysed reaction and to understand the mechanism of a reaction which is rather difficult in the case of heterogeneous catalysts. Homogeneous catalysts are discrete molecules containing one or more transition metals and their surrounding ligand. These organometallic catalysts offer a number of potential advantages. With homogeneous system only one type of the active site is there, while in a solid state catalyst, different types of sites are present but only one or two are involved in the reaction.

TABLE - 1.1

Comparison of Homogeneous and Heterogeneous catalysts (3).

	Catalyst	
	Homogeneous	Heterogeneous
	Effectiveness	
Active centres	all metal atoms	surface atoms only
Concentration	small	high
Diffusion problems	not present	present
Corrosive problems	present	not present
Thermal stability	not stable	stable
	Reproducibility of catalyst preparation	
Structure	known	unknown
Stoichiometry	known	unknown
Modification possibility	high	small
Reaction conditions	mild	severe
Catalyst separation	in part costly	easy
Applications	limited	wide

Homogeneous catalysts are potentially more specific since its metal atom is in the same environment. Homogeneous reactions lend themselves to better conservation of energy and use of material. The study of homogeneous systems provide clues to the behaviour and functioning of heterogeneous catalysts which are inherently more difficult to elucidate.

The ability of a transition metal to acquire different valencies enables its complexes to act as effective catalysts. This is because in all catalytic reactions, the catalyst has to take part in the formation of different intermediates, where the metal centre has to undergo different oxidation state changes. The catalytic efficiency of a complex is controlled by various factors like: 1) the nature of the metal centre, 2) the nature of the ligand system around the metal centre, 3) the availability and the number of free coordination sites, 4) the geometry of the complex molecules and 5) the nature of the solvent used for catalytic experiments.

In spite of the advantages, the major disadvantage of the homogeneous catalysts is the problem of the separation of the expensive catalyst from the products at the end of the reaction. This is easy with the heterogeneous catalyts. The techniques frequently used for the separation of the homogeneous catalysts are distillation or ion exchange process. The thermal stability of heterogeneous catalysts, such as pure metals and metal oxides, is often much higher than that of the homogeneous catalysts. The range of the suitable solvent for a homogeneous catalyst is often limited by the solubility characteristics of the catalyst.

1.2 Heterogenized homogeneous catalyst

The catalytic properties of most of the compounds are dependent on their ions and their immediate surroundings. It would therefore be ideal if the soluble catalyst could be immobilised on stable support without disturbing the active centres. The immobilised or the 'hetero-genized homogeneous catalysts' have now a days an active and attractive area of research (4-10).

The term '**heterogenized homogeneous**' is defined as the process whereby a transition metal is anchored to an inert polymer or inorganic support through covalent linkage. It is a new development of the catalyst and boundary between the homogeneous and the heterogeneous systems. This type of research provides the preparation of new types of the catalyst which can give a novel information on the origin of the catalysis. The major advantage of the supported metal complex catalyst is the easy separation from the reactants and the products and its re-use.

A homogeneous catalyst can be heterogenized in a variety of ways. The common method is to attach it to a solid support by adsorption or by an ionic or covalent chemical bond. Less common methods involve 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.

If the catalyst is heterogenized by a covalent linkage, it consists of the polymer support which is insoluble as well as inert to any solvent and the catalytic portion i.e. transition metal complex ions. The support and the catalyst both should be stable at the temperature and pressure required for the reaction under consideration. It is therefore important to use the ligands which after coordinating strongly give thermally stable complexes (11,12). An inert complex was found to be more stable than a labile complex. Chelated complexes are inert and less labile than non-chelated ones. A more stable metal complex 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 is lost. Very few cases of chelated catalysts have been reported, but there is no apparent reason why properly designed ones should not be as active as unchelated ones (13,76).

1.3 Types of Support

Two broad classes of supported complex catalyst 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 class, 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. In both cases mainly inorganic oxides and organic polymers have been used as supports.

1.3.1 Inorganic supports

The major advantages of inorganic supports over their organic counter parts are their better mechanical and thermal stabilities coupled with reasonable heat transfer properties. Very often the upper limit of the thermal stability of organic polymer supported complex catalysts is set by the polymer rather than the metal complex (14). Inorganic supports (77) that have been used include silica, alumina, glasses, clays and zeolites.

The rigid structure of the inorganic support can prevent the dimerization or trimerization which deactivates the catalyst in the homogeneous system. The average intermolecular interaction between anchored complexes may be controlled by immobilization on inorganic surfaces. Well characterized metal complexes containing anchoring ligands prepared in homogeneous medium may be supported on an inorganic substrate 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 intrinsic properties of the support (78).

Inorganic substrates can be selected for stable diffusional characteristics at most reaction conditions (15). Zeolites, with their well-understood controlled pore sizes, should be of particular value (16-19), although they have been studied relatively little.

However, the main disadvantage of the inorganic anchored catalyst is the leaching of the catalyst from the support to the solution. Immobilized transition metal catalysts may be unstable as a result of susceptibility to poisons.

1.3.2 **Organic polymer supports**

Three major types of the polymers have been used as supports: (i) Microporous polymers is a simple type of polymer, in which the long strands of polymer molecules are either lightly cross-linked or merely entangled randomly. (ii) Macroreticular or macroporous polymers have a carefully controlled regular cross-linking which allows a high internal surface area to the polymer (20,21). (iii) Popcorn polymers (22,23) are formed spontaneously in butadiene and butadiene copolymer plants. They are hard, porous and opaque materials which swell somewhat in benzene and carbon tetrachloride but are insolube in all common solvents.

Organic polymers that have been used as supports include polystyrene, polypropylene, polyacrylates and polyvinyl chloride. Polymers offer many advantages over other supports (24).

"Polymers, especially poly (styrene-divinylbenzene) can be synthesised with a wide range of physical properties. It can be easily functionalised particularly when polymers contain aryl groups (Figures-1.2, 1.3). Their porosity, surface area and solution characteristics could be altered by varying the degree of cross-linking (21,31,32). Unlike metal oxide surfaces, most hydrocarbon polymers are chemically inert and hence do not interfere with the catalytic group.

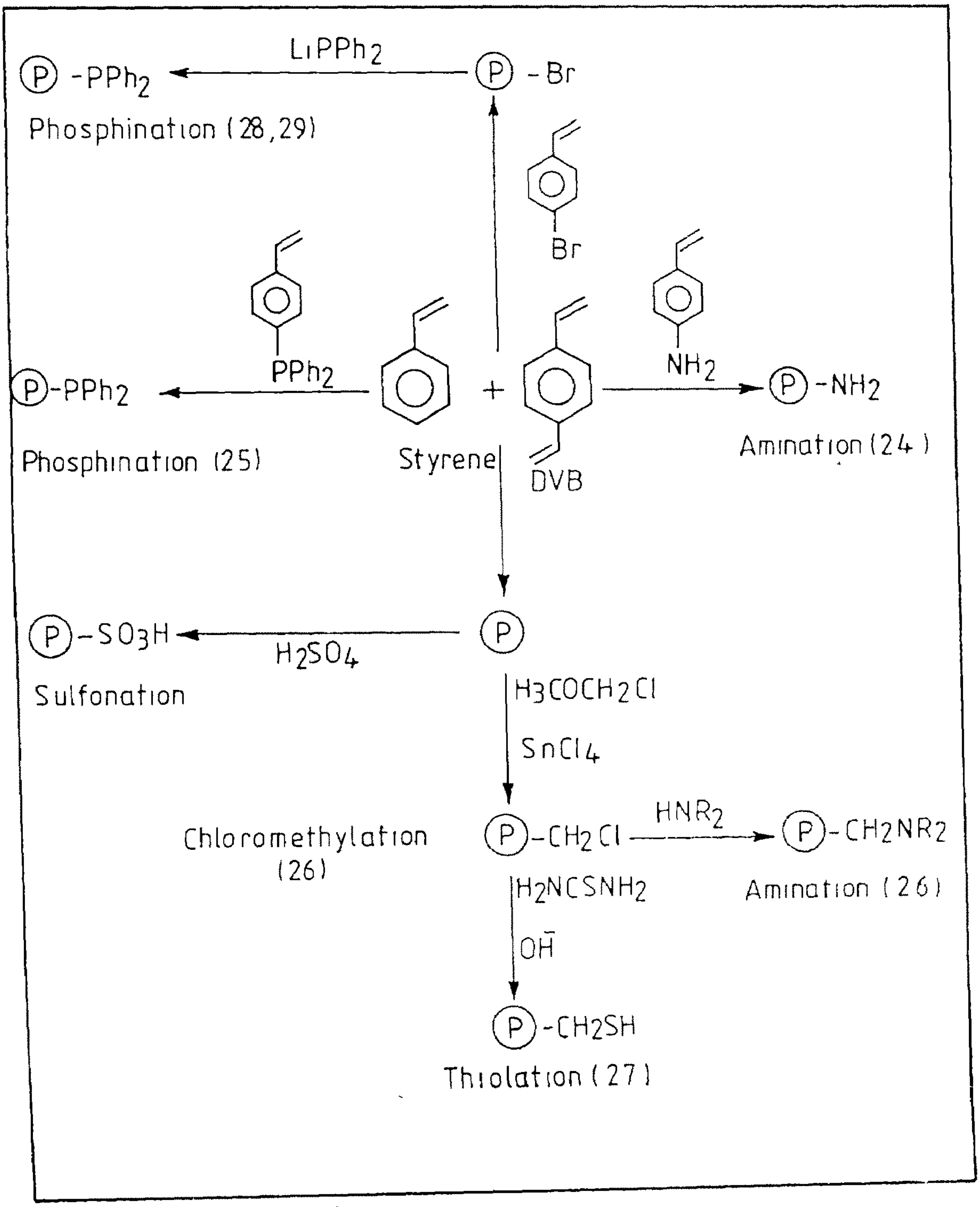

Figure-1.2 Preparation of functionalized polymeric supports

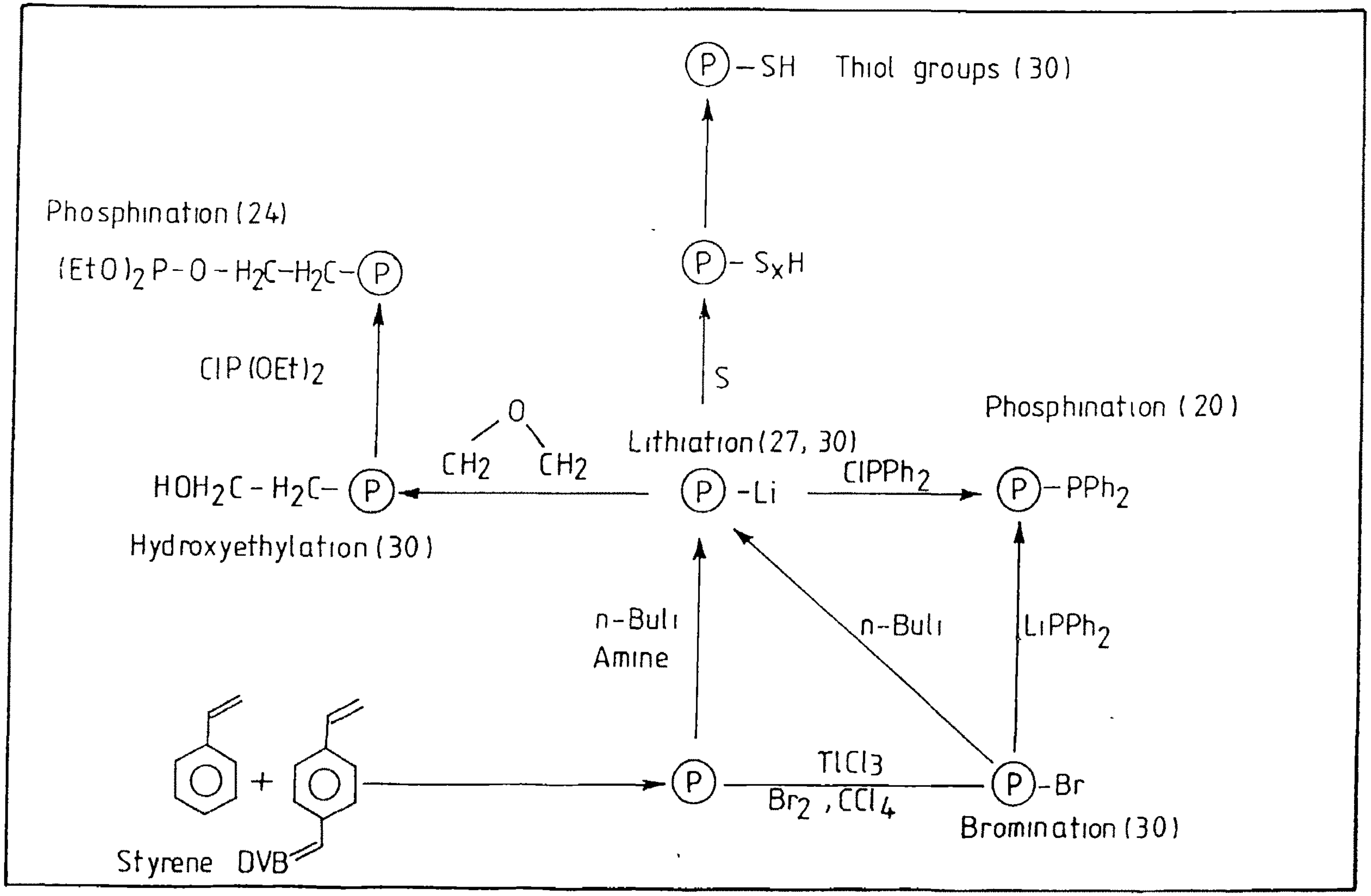

Figure-1.3 Preparation of functionalized polymeric supports

Another important attractive feature of organic polymer supports is the opportunity they offer to introduce extra selectivity into the catalyst through the control of diffusion of reactants with in the polymer. Common methods used to reduce the diffusion limitation of supported 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. Since diffusion within a polymer depends on the nature of the porous structure of the polymer, it is governed not only by the degree of cross-linking but also by the extent of swelling in the presence of the reactants and the solvents present.

The major disadvantages of polymers as supports are their poor heat transfer ability and in many cases their poor mechanical properties which prevent them from being used in stirred reactions in which they are pulverised. Recently polymers such as polypropylene (33-35) and poly (phenylene oxide) (36) have been studied specifically because they are mechanically strong. Although there are many attractions to using commercial polymers, these are not always very well defined and often contain unknown impurities. It is therefore important to develop the polymer supported catalysts which are well-defined and as pure a support as possible.

1.4 Aim and objective of the work

Platinum group metal complexes have received much attention in recent years because of the structural variety and their role in catalystic reactions such as hydrogenation (6,37-40), oxidation (41-45), epoxidation (46-49), hydroformylation (50,51), carbonylation (52,53), metathesis (54-56), polymerization (57-59) and isomerisation (60-62) of olefins. These complexes were also used in asymmetric synthesis (63), oxidative addition (64) reactions and the activation of small molecules such as O_2 (65), N_2 (66,67), H_2 (68), CO (69) and NO (70) within the coordination sphere of the metal ion.

The main objective of the thesis is to heterogenize the homogeneous transition metal complex catalysts and to investigate the catalytic activity for the industrially important reactions. The work is oriented towards the specific reaction namely the hydrogenation of cyclohexene and nitrobenzene using ruthenium(III) metal complex supported on poly(styrene-divinylbenzene) copolymer.

Homogeneous and heterogenized homogeneous catalytic hydrogenation of olefins have been studied using transition metal complexes. Ruthenium(III) complexes in homogeneous systems 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 especially on hydrogenation reactions either in homogeneous or supported systems(74). It has also been reported that the polymer anchored non-chelated complexes are less stable and leach out into the solvent(75). It was, therefore, planned to synthesize catalyst systems in such a way that the transition metal ions are attached with a chelated ligand introduced through a chemical reaction onto the polymeric support. Such systems are expected to be more stable( )

The present study includes :

(1) Synthesis of porous copolymer of styrene-divinylbenzene of various cross-linking and physical characteristics.

(2) Functionalization of the copolymer by the use of chloromethyl-methylether, introduction of the chelated ligand and finally treatment with the metal salt to form the appropriate metal complex on the polymeric support.

(3) Synthesis of the metal complex similar to the one attached to polymer support, for comparison of catalytic activity in homogeneous systems.

(4) Use of the commercially available copolymer (Zeo-Karb 226) as a support.

(5) Characterization of unbound and polymer bound catalysts using conventional techniques as well as spectroscopic methods in order to determine the probable structures.

(6) Investigation of the catalytic activity of these catalysts for hydrogenation using the two model reactions under various conditions.

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