CHAPTER 1

INTRODUCTION

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Catalysts are proven to be the backbone of the modern industrial progress and catalysis is believed to play very crucial role for future technologies. It has been estimated that in developed countries, catalysis contributes directly or indirectly through processes and products approximately 25% of Gross National Product (GNP) (1).

The chemical industries have a key position in overall global economy. Industrial production of various chemicals is based on catalytic processes. The use of catalysts allows the production of desired products with less environmental pollution due to minimization of by-products and a lower energy consumption (2).

In the context of globalization of all business activities, catalysis has become an intensive area of rapidly growing interest. The stringent ecological standards have compelled industry to opt for clean technologies. Therefore, only environmental friendly and economical technologies have become driving force behind new products and processes. This clean technology revolution in industry will obviously provide new opportunities for catalysis and catalytic processes (3) which can put more precision and elegance into chemical manufacturing (4). Therefore, it was identified as a thrust area in research.

In general, catalysts have been classified traditionally into two broad categories i.e. Homogeneous and Heterogeneous.

Homogeneous catalysts have been utilised in many industrial processes [Table 1.1] because of its various advantages (14) such as high activity and selectivity at mild operating conditions and availability of all the catalyst molecule to the reacting system. Nature of the active sites is better understood in case of homogeneous catalysts. It also offers advantages like stereospecificity, substrate activation and elimination of heat and mass transfer resistance. Their activity and selectivity can be tailored by varying the ligands attached to the metal.

Table 1.1 Applications of homogeneous catalysts

	Reaction / process	Catalyst	Product (Application)	Reference
1	Hydrogenation of maleic anhydride	Ru $(acac)_2$ phosphine complex	Butyrolactone (fine chemicals)	5
2	Asymmetric hydrogenation of 2-napthyl-4-methoxyacrylic acid	Ru-BINAP-chiral complex	S-Naproxen (pharmaceuticals)	6
3	Synthesis of α-tocopherol by asymmetric hydrogenation	Ru-BINAP	Vitamin E (pharmaceuticals)	7
4	Carbonylation of 2,4-dinitrotoluene	$Pd(Py)_2Cl_2$ or $Rh(Py)_3Cl_3$	Toluenediisocyanate (TDI)-intermediate for polyurethane (speciality chemicals)	8
5	Carbonylation of p-nitrocumene	$Rd(Py)_2\ Cl_2$ or $Rh(Py)_3Cl_3$	p-cumyl isocyanate-intermediate in pesticide-isoproturan (fine chemicals)	9
6	Selective hydrogenation of C-22/C-23 double bond	$Rh(I)(PPh_3)_3$	Ivermectin-antiparasitic drug (pharmaceuticals)	10
7	Hydrogenation of acetamidocinnamic acid	Rh-DIPAMP chiral complex	L-Dopa (pharmaceuticals)	11
8	Carbonylation of 1,4-diacetoxy butane	Rh-carbonyl iodide complex	Adipic acid (speciality chemicals)	12
9	Oxidation of indole	Cumyl hydroperoxide	Indigo (Dye stuff)	13

However, the main disadvantage of homogeneous catalysts is the problem of their separation from the reaction medium. Corrosion, plating out on the reactor wall and product contamination also pose serious problems. Catalyst handling and storage are difficult. It is deactivated easily due to the presence of trace impurities. Recycling and recovery of the homogeneous catalysts have also been found to be very expensive

A shift from conventional homogeneous to heterogeneous catalyzed processes is taking place due to their economical and ecological benefits (2). Apart from its ability to withstand high temperature and pressure, heterogeneous catalysts also offer easy handling, separation from reaction system, extended catalyst life as well as minimization of the formation of byproducts which save waste-disposal cost. They may be used in fixed beds in gas-solid and liquid-solid contact reactors (15). In this thrust towards transforming homogeneously catalyzed processes to heterogeneous catalysis, zeolitic catalysts are gaining an importance. The experience in the use of such catalysts in the petrochemical industry can be increasingly applied to the selective organic synthesis of chemical intermediates and fine chemicals. zeolites with their numerous adjustable catalytic properties offer a broad range of possibilities for this purpose. Vapour phase Beckmann rearrangement in the synthesis of ε-caprolactum and adipic acid is a good example of this fact. The conventional process offers high yield but due to use of sulphuric acid, a large amount of the side product, ammonium sulphate, is obtained which is an environmentally unacceptable drawback. The new synthesis route using H_2O_2 as an oxidant over a Ti-containing MFI-Zeolite TS-1 avoid the use of hazardous and corrosive sulphuric acid and the generation of ammonium sulphate (2).

Solid acid catalysts have also gained importance due to their high activity. Recently, an extremely active solid acid catalyst Nafion resin/Silica composite is developed at Dupont R and D for the friedel-crafts benzylation of benzene and p-xylene with benzyl alcohol. This composite catalyst was found to be nearly two orders of magnitude more active than plain Nafion resin (16). Catalysis by aerogels have also generated a lot of interest (17). Neumann et al. (18) have reported metal oxide substituted silicate xerogels as catalysts for oxidation of olefins using H_2O_2 as an oxidant. It was found that xerogels having porous structure with sufficiently large pores for fairly large organic substrates have the important potential as an active oxidation catalyst, valuable for the development of environmentally friendly processes. De Groot et al.(19) have reported production of phenol and acetone from cumene hydroperoxide with 100% selectivity using montmorillonite clay F-20 as a catalyst. Heterogeneous catalysts have also proved their importance in enantioselective reactions. Cinchona alkaloid modified platinum catalysts were found to be good catalysts for enantioselective hydrogenation of -α-ketoester by Blaser et al (20).

However, the advantages of heterogeneous catalysts, when compared to homogeneous catalysts, are at the expense of activity, selectivity and proper understanding of the nature of the active species. Thus, both homogeneous and heterogeneous catalysts have their own advantages as well as disadvantages. It is ideal, therefore, to combine the advantages and simultaneously minimize the disadvantages of each class of the catalysts. This can be achieved by heterogenizing a homogeneous catalyst i.e. attaching a homogeneous catalyst to a solid insoluble support. Here, the ligand sphere of the metal remains unchanged and the attached complex is bathed by solvent and reactants. Thus the resultant heterogenized homogeneous catalyst could function mechanistically as if it was in solution but it would operate as a separate immobile phase (15,21). The ideal catalyst thus obtained would have the specificity and controllability of the homogeneous type and separability of the heterogeneous system (22).

The supports used for these type of the catalysts can be classified into two categories.

1) Inorganic oxides such as silica, alumina, glasses, zeolites and clay etc.

2) Organic polymers such as polystyrene, polyvinylpyridine, polyacrylates etc.

Inorganic oxide supports have the advantages of better mechanical and thermal stabilities coupled with reasonable heat transfer properties. A number of studies have been reported on catalysis by inorganic oxide supported complexes (23). Many large scale industrial processes are catalyzed by such materials. Olefin polymerization using metal-oxide supported complexes of Cr, Ti or Zr; Paraffin hydrocracking using Pd supported on acidic zeolite, synthesis of formaldehyde by methanol oxidation using mixed oxides of Fe and Mo are some of the processes catalyzed by surfaces of inorganic solids (24). Many reports are available on application of mesoporous molecular sieve (MCM-41) supported catalysts for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), mild hydrocracking (MHC), friedel-crafts alkylation, olefin oligomerization and many other reactions including environmental catalysts (25). Recently Hu et al. (26) have reported partial hydrogenation of benzene to cyclohexene using ruthenium catalyst supported on La_2O_3-ZnO binary oxides and good results were obtained. Y. Kurusu (27) has reported immobilization of Fe(II) and Cu(II) ions on silica gel and montmorillonite clay using alkylaminotrialkoxysilane (SCR). These immobilized metal complex catalysts were found to have high activity towards oxidation of organic substrates under mild conditions. Armendia et al. (28) have reported use of spanish sepiolites as supports for palladium catalysts and its successful use in various reduction processes such as reduction of acetophenone and various substituted alkenes. El-Shobaky et al.(29) have found a low energy of activation in catalytic oxidation of carbon monoxide by oxygen using NiO/Al_2O_3 catalyst. Thus various inorganic oxides were found to be good catalyst supports.

Organic polymers were also found to be popular catalyst supports. A brief outline on the emergence, advantages and applications of polymer supported metal complex catalysts is given in the following section.

1.2 Polymer supported catalysts

The use of polymer supports for catalysts as well as for synthetic reagents has grown tramendously since Merrifield demonstrated their use in peptide synthesis (30).

Attachment of transition metal complexes to organic polymers appeared by the end of 60's as a suitable means to approach two of the main goals (31) of research groups in catalysis:

1) Formation of stable catalysts with reproducibility, activity and selectivity as homogeneous systems and separation from reaction products as heterogeneous catalysts.
2) Achievement of a catalyst system where the active sites have known structures which may permit better understanding of the molecular mechanism of the catalytic reaction.

To prepare polymer supported catalysts usually transition metal complexes are covalently attached to polymeric networks to make them insoluble in the reaction mixture. For this purpose, functional polymer support is synthesised either by polymerizing the monomer containing desired functional groups or by functionalizing cross-linked polymer and then incorporating metal complex catalyst precursor on to this functionalized polymer support.

There are many advantages of using polymers for supporting metal complexes. Polymer supports are insoluble, non-volatile, non-toxic and often recyclable. These properties are especially attractive in an era of enhanced environmental awareness (32). Most of the polymers used as supports are found to be inert and do not interfere in catalysis. These polymers can be synthesised easily with a wide range of physical properties Their functionalization capacity could be increased by introducing the aryl groups (33). In fact, degree of functionalization is a significant difference between inorganic oxide and organic polymer supports. Inorganic oxides have an upper limit of monofunctional groups of 1-2 meq per g of matrix. Organic matrices can carry up to 10 meq per g of matrix (24). Thus, compared to inorganic oxides, organic polymer supports can offer immense modification possibilities.

By preventing deactivation of reactive catalytic species, polymer supports stabilize the unstable structure on the surface. The catalytic solution of Wilkinson's complex, $RhCl(PPh_3)_3$, loses its activity upon exposure to air. When the complex is supported on polystyrene resin, it can be employed in air without its getting deactivated (34). Dimerization of the catalyst in the reaction mixture could be prevented due to isolation of the active sites on the polymer matrix. Thus supported catalyst can be prepared with high dispersion of metal atoms in polymer matrices, in order to achieve optimum reactivity and selectivity. The role of the polymeric ligand is to stabilize reduced metal species and prevent formation of metal aggregates. Othaki et al.(35) immobilized ultrafine Rh particles protected by a copolymer of methylacrylate and N-vinyl-2-pyrrolidone, P(MA-VP), on polyacrylamide gel by forming an amide bond between the primary amino group of the support and the methyl acrylate residue in the protective polymer. A better catalytic activity compared to homogeneous species was observed using these immobilized complexes towards olefin hydrogenation (35). This is due to the dispersion of metal atoms in polymer matrices. Life time of highly reactive intermediate could be increased by matrix-immobilization (36). Polymer supports stabilize the reactive and co-ordinatively unsaturated metallic sites, thereby increasing the activity of the catalyst. Presence of metal complexes with a vacant ligand site in polymer-bound catalyst enhance its activity. Such situation can rarely occur in homogeneous complex. Braca et al.(37) have proved the presence of coordinatively unsaturated Rh(I) sites with the help of IR and ESR spectra in hydrogenation and isomerization of olefins under mild conditions using polymer-bound Rh(I) catalyst.

In polymer-anchored catalysts, phosphine complexes are often used to tie the metal to the solid support because homogeneous catalysis with metal phosphine complexes is an attractive area of research (38). Hydrogenation, Isomerization, Oligomerization, Hydroformylation etc. reactions using metal catalysts heterogenized on phosphinated polymer are reported with better activity as compared to homogeneous counterparts (39-46). However, such catalysts were found to be air sensitive (47).

Application of non-phosphinated polymer-bound catalysts in different catalytic processes like Oxidation (48-51), Hydrogenation (47,52--59), Isomerization (60,61), Epoxidation (62), Hydroformylation (15, 63-64), Carbonylation (65-66), Oligomerization (67) etc. are available in open and patent literature. These polymer-bound catalysts have been reported to be more reactive and selective than their homogeneous counterparts. Many attempts have been made to explain their enhanced reactivity. Matrix-isolation of catalytic sites, coordinative unsaturation, prevention of deactivation of reactive catalytic species etc. were found to be the cause behind enhanced activity. Choice of better swelling agent also helps to promote activity (68-71). Thus polymer supported catalysts were found to be suitable in many synthetic applications. However, each system must be studied and optimized independently (15).

Polymer-supported catalysts were also found to be useful in multistep catalytic reactions (72-73). Polymer-supported phase transfer catalysts (PSPTC) has been widely used in organic synthesis to minimise the loss of the catalyst (74-75). Recently Balkrishnan and Murugan (74) have prepared surface enriched polymer-supported phase transfer catalysts (SE-PSPTC) using vinyl toluene (VT) as a functional monomer. These catalysts were found to be effective in dichlorocarbene addition to cyclohexene under mild conditions. Polymer supported enantioselective catalysts were also studied extensively (76-77). Nguyen and Grubbs (78) have recently observed that polystyrene supported olefin metathesis catalysts based on $Cl_2(PR_3)_2Ru=CH-CH=CPh_2$ are effective compared to their homogeneous analog. These catalysts can be recycled and reused. Jose and Pillai (79) have observed catalase-like activity of Divinylbenzene (DVB) cross-linked polyacrylamide supported amino metal complexes in H_2O_2 decomposition.

Thus the development of viable polymer-bound catalyst for laboratory and industrial application has gained prominence in research (80-84). Ion-exchange resins based on sulfonated polystyrene have been used as catalysts in a number of industrial processes, including synthesis of methyl t-butyl ether (MTBE), t-amyl methyl ether (TAME), bisphenol A, methylvinylketone, isoamylene, dianone and phenol alkylation (85). These resins have also been employed as supports for metal crystallites. Supported palladium catalyst of this kind (Bayer K 6333) is currently used extensively for the removal of oxygen to bring down to the ppb level from water to be used in power plants (85). Moreover, polymer matrices are now utilized on industrial scale as supports for enzymes in biocatalyzed processes such as the synthesis of aspartic acid and fumaric acid (Tanabe Seiyaky) (86), of lactose-free milk, 6-amino penicillanic acid (Snamprogetti) (86) and for the conversion of acrylonitrile into acrylamide (87). This relatively new area of application is thus rapidly expanding (88-89).

1.3 Polymer-anchored Pd(II) and Ru(III) complexes as hydorgenation/oxidation catalysts

The catalytic hydrogenation of organic functional groups is probably the most common application of catalysis in the synthesis of organic compounds. The usefulness of this reaction is well covered by texts, reviews and conference proceedings (90). Catalytic oxidation of organic molecules has been a subject of renewed interest in recent years because the catalytic reactions are environmentally safe and could replace stoichiometric oxidations. Products of these reactions are very important as end products or intermediate in fine chemicals, pharmaceuticals and many other industries. Application of polymer-bound Pd(II) and Ru(III) complexes in these reactions have been extensively covered in literature. Homogeneous complexes of these ions were found to be very versatile catalysts and it was thought that by heterogenizing them on polymer supports, their activity could be enhanced (56). Zhang et al.(91) have observed that Ion-exchange resin supported $PdCl_2$ has better catalytic activity for the hydrogenation of cotton-seed oil as compared with $PdCl_2$ supported on carbon. Xavier and Mahadevan (47) have reported polymer-supported Pd(II) catalysts which were found to be effective for the reduction of alkenes, dienes, alkynes and nitroaromatics under mild conditions. Kaneda et al.(56,58) have reported various organic reactions including hydrogenation catalyzed by polymer-bound palladium complexes and found them to be effective catalyst which can be reused with small loss of catalytic activity. Catalytic air oxidations of alcohols by polymer-bound Pd(II) complexes is recently reported by Noronha et al. (48). Zhao et al.(92) have heterogenized Ru(III) complexes on chloromethylated polystyrene-divinylbenzene using binuclear ligands and observed a higher activity and selectivity for the hydrogenation of diacetone alcohol. Jia et al.(93) have observed high activity of polymer-triruthenium cluster catalysts in the oxidation of styrene under very mild conditions. The bimetallic complex catalysts supported on polymer were also found to be very effective. Yu et al.(94) have reported the hydrogenation of nitroaromatics using polymer anchored Pd-Ru and Pd-Pt catalysts. Better catalytic acitivity found under relatively mild conditions in all these studies shows that polymer-bound Pd(II) and Ru(III) complexes are very valuable catalytic materials which have generated a lot of interest in catalytic community. Studies were also carried out to investigate relationship of physico-chemical properties of polymer-bound catalysts with their activity (95). Such studies have helped to improve this class of catalytic materials. Ram et al.(52,69-70,96-97) have studied a number of polymer supported Pd(II) and Ru(III) catalysts using 1,2-diaminopropane (DAP), trimethylenediamine (TMDA), glycine and L-2-aminobutanol (L-2AB) as ligands and found them to be effective towards hydrogenation and oxidation of olefins compared to homogeneous counterparts. However, leaching of metal ions from the surface of the polymer was found to be a problem with some of these catalysts. It was therefore planned to use highly functionalized commercial polymer as supports and multifunctional ligands with N and O as donor atoms to prepare polymer-bound catalysts for present investigation.

1.4 Aim and objective of the work

The main aim of the present work is to heterogenize the homogeneous transition metal complex catalysts and to investigate their catalytic activity for hydrogenation and oxidation reactions. The work is focussed on hydrogenation of 1-hexene/styrene as well as oxidation of benzyl alcohol using palladium(II) and ruthenium(III) complexes of Salicylaldehyde-ethylenediamine (Salen) and Ethylenediaminetetraacetic acid (EDTA) anchored on to various cross-linked styrene-divinylbenzene copolymer.

The present study includes

1) Functionalization of styrene-divinylbenzene copolymer of different cross-linking by chloromethylation, treatment with multidentate ligands containing N and O as donor atoms and finally attachment of Ru(III) and Pd(II) metal ions to form appropriate metal complexes on the polymer matrix and alternatively, use of commercially available chloromethylated styrene-divinylbenzene as support. It is believed that highly functionalized copolymer (extent of chloromethylation 17.5%)

will give rise to strongly bonded metal complexes to prevent or reduce metal leaching.

2) Synthesis of the chelated metal complex similar to the polymer-anchored metal complexes to study the catalytic activity in homogeneous system.
3) Characterization of synthesised catalysts using different techniques such as Infrared, UV-vis reflectance, Electron spin resonance spectroscopy; X-ray photoelectron spectroscopy (or ESCA); Thermogravimetric analysis (TGA) Scanning electron microscopy (SEM); Swelling studies using different solvents; Surface area measurement using BET method at liquid N_2 temperature and other physico-chemical studies like moisture content, bulk density etc. Attempt to propose possible structure of catalysts on the basis of the modern spectroscopic techniques.
4) Investigation of catalytic activity of the synthesised catalysts for the hydrogenation of 1-hexene/styrene as well as oxidation of benzyl alcohol under mild operating conditions.
5) Comparison of catalytic activity of homogeneous and heterogenized homogeneous catalysts.
6) Life cycle studies of heterogenized catalysts.
7) Investigation of probable reaction mechanism for both the systems.

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