CHAPTER I

GENERAL INTRODUCTION
1.1 INTRODUCTION

Civilization has traversed a path of astonishing progress and has made rapid strides of development in the twentieth century. In order to achieve this development, it was necessary to invent a number of new materials and to evolve ways and means for their fast and cheap production in large quantities. The development of the science and practice of catalysis has opened up new vistas for the fast and selective production of desired chemical molecules. This scientific revolution has triggered the advent of molecular design techniques which have unlimited scope and potential to provide for the most basic of all human needs—health, food, energy and materials. The dictum that underlines all catalyst research is the development of cost effective methods that have an inherent commitment to environmental sustainability. Catalyst technology has become all pervasive in our society and includes in its domain enzymes (biocatalysts), pharmaceuticals, petrochemicals, energy, plastics and fibers and what not.

1.2 RECENT TRENDS IN CATALYSIS

Catalysis is directly or indirectly involved in almost all processes in modern industries. In early days, the preparation of heterogeneous catalysts and their operation were considered to be more an art than a science. Later, with the advent of modern sophisticated surface science techniques, catalysts and catalyst based technologies have undergone tremendous changes. A catalyst is a surface active material i.e. catalysis occurs at the surface of the catalyst and hence the activity of the catalyst depends very much on the nature of its surface. The performance of industrial catalytic processes is determined not only by the activity of the catalyst but also the process parameters like nature of feed and operating conditions such as temperature, pressure, space velocity, etc. All these factors ultimately determine the exact nature of chemical species and their relative concentration on the catalyst surface under actual process conditions. Recognizing the exact nature of these surface species and fine tuning them for still better catalytic performance are the main objectives of catalyst-research.
The rapid growth of human population and high standard of living of modern society necessitate considerable enhancement in the production of materials. Increased production results in an increase of undesirable by-products and therefore in elevated levels of environmental pollution. Therefore, chemical technology focuses on developing novel environment-friendly catalysts that can provide high selectivity leading to minimum toxic effluents, without sacrificing on yield and energy requirements. The development of a three-way catalytic converter for controlling auto exhaust emissions, application of molecular sieves for better selectivity and alternative chemical routes via catalytic oxidation, hydroxylation, etc. for fine chemical are some of the achievements of these efforts.

Progress in the science of catalysis and its industrial applications is highly essential to cater to the demands of modern society. In order to achieve this it is necessary to replace present technologies with new, energy-efficient, environment-friendly catalytic processes of high selectivity. This quest has triggered a renewed interest in metal complexes which are known to exhibit remarkable catalytic properties. Furthermore, the heterogenization of homogeneous catalysts has also received considerable importance as it avoids the technical problems in using homogeneous catalysis, but preserves the catalytic performance.

1.3 CATALYSTS IN INDUSTRY

Traditionally, industrial catalysts have been classified as homogeneous and heterogeneous. Metal complexes and organometallic compounds are the important homogeneous catalysts. These catalysts are soluble in the reaction medium and are used in the production of high purity, high value chemicals. Usually, homogeneous catalytic reactions are very complex and proceed as a closed cycle of linked chemical reactions which involve different intermediate species. However, they exhibit high efficiency and selectivity and operate at milder conditions of temperature and pressure. Moreover, homogeneous catalysts of definite stoichiometry and structure can be easily made with more reproducibility. In contrast to homogeneous catalysts, heterogeneous catalysts are
usually solid surfaces or species attached to solid surface. They are mainly used for the production of large scale commodity chemicals such as methanol and ammonia and in the production of gasoline from petroleum.

Both homogeneous and heterogeneous catalysts were extensively used in industry since the beginning of the twentieth century. But, heterogeneous catalysis has grown at a faster rate than homogeneous catalysis in industry. The main technical problem in the use of homogeneous systems is the separation of catalysts from reactants and products, which is practically very easy in the case of heterogeneous catalysts. The deactivation of homogeneous catalysts by the self aggregation of the active sites may also restrict its application in industrial processes, whereas heterogeneous catalysts are relatively more stable. The above mentioned facts may be the reason for the tardy growth of homogeneous catalyst systems in industry. However, the ability of homogeneous systems to catalyse a variety of specifically designed chemical transformations promises lot of scope for future developments.

1.3.1 Homogeneous catalysts

One of the first industrially applied homogeneous processes is Oxo process discovered by Otto Roelen in 1938. In this process, the hydroformylation of olefins occurs in presence of carbon monoxide and hydrogen at 140-180 °C and a pressure of 200-300 atm over cobalt hydride carbonyl complexes. Later, this catalyst was modified with trialkyl phosphine to lower the reaction pressures and to obtain higher selectivity. The technical importance of this process is because the primary reaction product, the aldehyde, can be easily converted to industrially important secondary products like alcohols, acids, diols, amines or esters.

Another interesting achievement in this field was the use of Reppe reactions for the commercial production of various chemicals. This reaction involves the addition of a base to olefinic or acetylenic C-C bond with simultaneous insertion of CO. The synthesis of acrylic acid from acetylene, CO and water with activated nickel carbonyl catalyst.
HNi(CO)\textsubscript{X}, is one of such reactions. Reppe carbonylations also include reactions such as propionic acid from ethylene and water, and acetic acid from methanol.

Catalysis by protons using acids (H\textsubscript{2}SO\textsubscript{4}, BF\textsubscript{3}, H\textsubscript{3}PO\textsubscript{4}) was employed to a large extent in alkylation reactions, for example, in the production of alkylated gasoline from isobutylene and in the production of cumene, xylene and styrene from benzene \textsuperscript{6}. A similar acid catalysed reaction is Koch synthesis \textsuperscript{6} in which olefins and other compounds readily react with CO and water or alcohol to produce carboxylic acid or corresponding ester respectively. The carboxylic acids formed from isobutylene, diisobutylene and from mixture of olefins in the range C\textsubscript{6}-C\textsubscript{10} are used as starting materials for resins, lacquers and synthetic lubricating oils.

Another significant discovery in the field of homogeneous catalysis was the development of Wacker process for the production of acetaldehyde from ethylene \textsuperscript{13}. Soluble metal complex salts like palladium(II) chloride were used as catalysts for this process. This catalyst operates at 10.5 atm and 125-130 °C to obtain a yield of 95%. Wacker process is widely accepted in industry as it replaced expensive acetylene with cheap ethylene for the manufacture of acetaldehyde.

Rh complexes have been found to be more efficient catalysts than that based on cheaper and abundant metals. One of these complexes, RhCl(PPh\textsubscript{3})\textsubscript{3}, widely known as Wilkinson's catalyst, can be used for the hydrogenation of olefins \textsuperscript{14}. Also, the complexes such as RhH(CO)PPh\textsubscript{3} catalyse hydroformylation of propene to n-butraldehyde at 10-20 atm and give a yield of > 90% for the linear product, whereas Co\textsubscript{2}(CO)\textsubscript{8} catalyst performs this reaction only at high pressures (~200 atm) and produces a lower yield of 70% \textsuperscript{15}. Monsanto's rhodium catalysed carbonylation of methanol to acetic acid is also very attractive as it replaces conventional high pressure processes with low pressure ones and shows a high selectivity \textsuperscript{16}. A similar example is the use of rhodium complexes for oxo-process in presence of triphenylphosphine as co-catalyst \textsuperscript{6}. The advantages of this rhodium based oxo-process are lower operating pressure and better selectivity for straight chain product.
Olefins and dienes can be oligomerised by means of homogeneous catalysts under mild conditions. The Esso process with alkyl aluminium chloride and titanium tetrachloride, the shell process with nickel-phosphine catalysts, and the Ethyl process with the classical Ziegler trialkylaluminium catalyst are some of the industrially important homogeneous processes for ethylene oligomerisation. Homogeneous oxidation catalysis is also known, for example, cyclohexane to adipic acid, butane to vinegar, propylene to propylene oxide and p-xylene to terephthalic acid. Furthermore, the direct addition of hydrocyanic acid to butadiene can be performed over nickel(0) phosphine or phosphite complexes at atmospheric pressure and 30-150 °C.

Besides above established homogeneous processes, some relatively new catalytic processes were developed and commercialized. The application of Wilkinson's metal complex to selectively hydrogenate biologically active substrates like steroids is an excellent example for such achievements. In addition, Monsanto has introduced a process using Wilkinson's catalyst for producing L-dopa (3,4-dihydroxyphenylalanine), an effective drug against Parkinson's disease. The introduction of this process was highly significant as it was a classic example for the application of homogeneous catalysts in the synthesis of fine chemicals and also it is one of the most selective catalytic reactions known. Some of the recent studies have focused on the use of homogeneous catalysts for regioselective and enantioselective reactions. Since homogeneous catalysts are generally active at low temperatures, more new developments can be expected in this area. There is scope for new catalysts and new reactions in wake of energy and raw material considerations that will determine the direction of worldwide developments in chemical technology.

1.3.2 Metal oxide catalysts

Heterogeneous transition metal oxide catalysts are extensively used for various industrial applications where working conditions are more economical. A number of such systems like mixed metal oxide, perovskites, spinels, etc. were reported to be active for several reactions. Also, there is a pronounced interest for replacing highly
expensive noble metal catalysts with metal oxide alternatives. Main attraction of metal oxide systems is the low cost and easier methods of preparation as compared to that of other catalytic materials.

Many of the recent studies show that the performance of an industrial catalyst with respect to activity and selectivity depends greatly on the nature of the active sites formed on the catalyst surface during pretreatment or as a consequence of the catalytic reaction on it. The newly developed sophisticated surface science techniques provide valuable informations on the nature of active sites and their influence on catalytic activity. The application of such techniques was reviewed by several authors. Furthermore, the physical properties like thermal and mechanical stability, surface area, porosity, shape, dimension, etc. are to be optimised for the successful operation of catalytic processes in industry.

Iron catalyst for ammonia synthesis is one of the classic industrial catalysts. A quite large number of studies have been conducted using a combination of surface techniques to characterize this catalyst. The catalytic synthesis of methanol has gained considerable importance in the wake of energy crisis as it can be used as a starting material for the synthesis of various chemicals. A catalyst consisting of CuO and ZnO on alumina support is presently used for the manufacture of methanol. CuO-ZnO/Al₂O₃ catalyst is also used for water gas shift reaction in fertilizer plants. Supported nickel oxide catalyst is used for the steam reforming of hydrocarbon feedstocks like naphtha, LPG and natural gas into methane for its further conversion to hydrogen, ammonia, ammonia based fertilizers and methanol.

γ-Al₂O₃ supported oxides of Mo or W, promoted with oxides of Co or Ni are used for the hydrotreating of petroleum fractions. The bulk preparation of styrene, one of the most important monomers in modern petrochemical industry, is based on the dehydrogenation of ethylbenzene over potassium promoted iron catalyst. Some of the other catalytic processes in this class are ammonoxidation of propylene to acrylonitrile over silica supported bismuth-molybdate catalyst, oxidation of methanol to
formaldehyde over iron molybdate, hydrolysis of acrylonitrile to acrylamide and hydrogenation of nitrobenzene to aniline over Cu based catalysts, oxidative coupling of methane by Li doped MgO, Fischer-Tropsch synthesis over CuO-ZnO/Al₂O₃ catalysts, Claus process by alumina catalysts, V₂O₅/TiO₂ catalysed oxidation of o-xylene to phthalic anhydride and selective catalytic reduction of NOₓ over V₂O₅/TiO₂/SiO₂ catalyst.

1.3.3 Noble metal catalysts

Supported noble metal catalysts have found numerous applications in industries because of the advantages such as high specific activity and mild reaction conditions compared to metal oxide systems. Another attractive feature of noble metal catalysts is the ability to enhance the productivity in industrial processes. However, there are some disadvantages in the use of noble metal catalysts. They are relatively scarce and therefore expensive, and sensitive to impurities due to low amounts of metal present in the catalyst. High volatility and ease of oxidation of noble metals are the other problems encountered in their commercial use. In spite of these disadvantages, noble metal catalysts are the best choice for a number of applications where transition metal oxides have failed to remain efficient in hostile environment like high temperature, numerous poisons and fluctuating gas compositions.

Automobile exhaust catalysts comprise a complex formulation composed of precious metals like Pt, Pd & Rh, additives like CeO₂ and alumina stabilized with La₂O₃. The support and active components are dispersed on a monolith structure for the effective control of emissions from automobiles. Catalysts containing Pt or Pd were used for the high temperature combustion of flue gases. In 1991, British Petroleum and Kellogg announced the development of a new process for ammonia synthesis using ruthenium supported on a high surface area graphite carrier as catalyst. Bimetallic Pt-Re catalyst is used for the reforming naphtha or other petroleum fractions with low octane number to gasoline fractions with higher octane number or to aromatic feedstocks for petrochemical industry. Selective hydrogenation of acetylenes to
corresponding olefins in C₂, C₃ and C₄ petrochemical streams is generally carried out on different types of supported Pd catalysts⁴⁵.

Supported Pt catalyst is used for the dehydrogenation of paraffins to olefins¹⁰. The use alumina supported Ru catalyst for the effective conversion of glucose to sorbitol was reported⁴⁶. A Pt-Rh alloy catalyst is used for the oxidation of ammonia to NO/NO₂ in the manufacture of nitric acid⁴⁷, ⁴⁸. Another important applications of noble metal catalysts are industrial gas purifications such as deoxo process⁴⁹, ⁵⁰, oxidation of CO to CO₂⁵¹, ⁵², etc. CO oxidation over noble metal catalysts is generally identified as structure sensitive reaction and the reported structure sensitivity is higher for Pd which shows higher activity than Pt⁵³.

1.3.4 Zeolites & Zeolite based catalysts

Catalysis by zeolites has been extensively studied for a broad range of reactions in the past few decades³, ⁵⁴-⁵⁷. The characteristic features that make them attractive as heterogeneous catalysts are well defined crystalline structure, uniformly arranged pores with one or more discrete sizes, high internal surface area, good thermal stability, highly acidic sites when ion exchanged with protons, well dispersed metal sites on ion exchanging with metal cations and reproducibility of various forms. In general, zeolite catalysis involves both acid catalysed reactions and other chemical transformations. The former is due to the confinement of acid sites in zeolite pores, whereas the latter is the result of presence of ion exchanged metal sites along with the acidic sites. The major achievement in the field of zeolite catalysis was their introduction as cracking catalysts by Mobil in 1959⁵⁸.

The advantage of molecular sieve catalysts over amorphous silica-alumina is size/shape selectivity. This remarkable feature of zeolites has been exploited to perform many large scale selective reactions in the field of petroleum refining, petrochemical manufacture, synfuels production, NOₓ abatement and fine chemical industry⁵⁸. Generally, zeolites show four types of selectivities. They are: (1) reactant selectivity
when pore size limits the entrance of reacting molecules, (2) product selectivity when some of the product formed within the pores are too bulky to diffuse out, (3) restricted transition state selectivity when certain reactions are prevented due to the non-availability of required space for corresponding transition state and (4) molecular traffic control in zeolites with more than one type of pore system. Reactant molecules enter the zeolite through one type of pore system while products diffuse out through the other type of pore.

The invention of new zeolite materials has enabled the development of improved technologies for the successful production of various chemicals. For instance, extra large pore molecular sieve catalysts were developed to perform shape selective catalysis on reactants too large to enter the pores of large molecular sieves. This idea was illustrated in some liquid phase and vapour phase reactions. Furthermore, the catalysts produced by modifying nonacidic molecular sieves with acidic guest materials were found industrial applications for shape selective base catalysis. This material has also been used for the industrial production of some chemicals in environmentally friendly manner as compared to conventional catalytic processes which involve several hazardous intermediates.

Metal exchanged zeolites are known to catalyse a variety of oxidation reactions. Among them, titanium containing zeolite is a unique material that can catalyse a broad range of oxidation reactions. Another interesting system is vanadium exchanged zeolites which was found to be effective for high temperature oxidation, oxyfunctionalisation, oxidation of NO with oxygen, etc. In addition, the recent importance of enantioselective synthesis has lead to the development of zeolites that can perform shape selective, asymmetric, heterogeneous catalysis.

1.4 TOWARDS HETEROGENIZING HOMOGENEOUS CATALYSTS

Although, homogeneous catalysts show excellent catalytic properties, their applications are limited as they are difficult to separate from the reaction medium.
Attempts have been made to combine the high activity and selectivity of homogeneous catalysts with operational benefits of heterogeneous catalysts by heterogenizing known homogeneous catalysts. Several approaches have been considered for this purpose, which can be classified into two. They are:

1) *Heterogeneous molecular catalysts* - prepared by methods which induce rearrangement of ligands around the metal center.

2) *Supported homogeneous catalysts* - prepared by methods which preserve the structure of metal complex as much as possible.

### 1.4.1 Heterogeneous molecular catalysts

Heterogeneous molecular catalysts are prepared by anchoring the organometallic complex through a direct bond between the metal center and a surface atom. This direct linkage leads to changes in the coordination environment around the metal center. The structure of supported complex can be very different from the precursor complex to obtain entirely new heterogeneous organometallic catalyst. Metal carbonyl clusters anchored on silica support are good example for this class of catalysts. Although, the reactivity of this system is promising, it has only limited scope for industrial applications since they are very unstable towards degradation under reaction conditions. Heterogeneous molecular catalysts of Re were synthesized by supporting its complexes on inorganic carriers like alumina, alumina-silica and niobia and were studied for the metathesis of olefins. Even though, these complexes have shown catalytic activity, the presence of variety of surface species restrict them to be well defined.

### 1.4.2 Supported homogeneous catalysts

In supported homogeneous catalysts, the structure of the metal complex is almost identical to that of the precursor homogeneous catalyst. For this kind of heterogenization, many different approaches have been considered which belong to three classes. They are:
1) Catalysts anchored on functionalised solids
2) Supported liquid phase catalysts
3) Encapsulated, intercalated or entrapped catalysts

(1). Catalysts anchored on functionalised solids

Homogeneous catalysts are anchored to an inorganic oxide or an organic polymer by bonding the solid with one (more) ligand(s) at a position away from the atom coordinated to the metal center. These systems can be synthesized in two ways. The first method consists in functionalising the support by reacting its surface with a bifunctional ligand and then the metal complex is supported by a ligand exchange reaction with surface groups. For example, the anchoring of phosphine complexes to polymers is done by chloromethylation of phenyl rings of the polymer by chloromethyl ethers, then functionalising by reacting with LiPPh₂ and exchanging with homogeneous catalyst 14. In the second approach, a metal complex containing desired amount of functionalised ligand reacts with the solid surface to form the supported complex. Ni(CO)₄, as an example, was anchored by reacting it with phosphinated silica at optimum experimental conditions 77. Supported homogeneous catalysts were tested for a number of industrially important reactions. Although the catalytic activity of these catalysts is as good as their homogeneous counterparts, the disadvantages including leaching of metal complex in liquid phase reactions and aggregation to form binuclear species restrict its usage in industry 77.

(2). Supported liquid phase catalysts

Catalysis in biphasic media is one of the efficient methods to solve the problem of catalysts separation from reaction medium and therefore this technique has found a number of applications 78-82. However, this method is not effective when the solubility of reactants in catalyst phase is too low and hence activity is too low as a result of lower interfacial surface. In such cases, supporting the catalyst in a thin film of nonvolatile liquid deposited on a solid of high specific surface area improves significantly the
activity. The isomerisation of pentene-1 catalysed by RhCl supported in a thin film of ethylene glycol and hydroformylation of propene catalysed by (Ph₃P)₂Rh(CO)Cl in benzylbutylphthalate film are some examples of supported liquid phase catalysts. Supported aqueous phase catalysts were developed by supporting water/organic solvent biphasic catalysts. However, a complete evaluation of the catalytic properties of supported liquid phase systems, such as kinetic analysis, recycling tests, metal leaching, etc. has to be performed to scale up this class of catalysts to industrial applications.

**Encapsulated, intercalated or entrapped catalysts**

Transition metal complexes can be immobilized in the voids of a porous inorganic or organic solid by encapsulation, intercalation or entrapment. A variety of compounds have been encapsulated in the porous network of preformed solids mostly in large zeolites. In contrast to those supported on nonporous inorganic oxides, zeolite encapsulated complexes are stable under reaction conditions due to reduced dimerisation or aggregation. Additionally, more selectivity is also induced via steric effects of the zeolite framework.

Intercalated catalysts are prepared by introducing cationic complexes as such between the silicate layers of swelling clays, such as smectites by ion exchanging. The increase of interlayer spacing provides evidence for intercalation. The enhanced selectivity of intercalated catalysts in reactions indicates the presence of steric effects. The special feature of this system is the possibility to adjust the size of interlayers by incorporating complexes of different sizes, whereas zeolite pores are rigid.

In the case of entrapped catalysts, metal complex is introduced directly in the mixture of reactants used for the synthesis of the solid support. A number of entrapped complexes were prepared and successfully tested for reactions such as hydrogenation, isomerisation and hydroformylation. It is possible to obtain good activity, selectivity and stability for such systems by the simultaneous choice of the metal complex and support in such a way that it allows the diffusion of reactants and products.
EMERGING FRONTIERS IN HETEROGENIZATION-
ZEOLITE ENCAPSULATION

The great interest in zeolites arises from their well defined structures that are attractive for designing new efficient catalysts. The steric constraints imposed on the reactants in the channels and cages of zeolites can lead to new reaction pathways which are easier as compared to those on conventional systems. Thus, the architecture of zeolite provides opportunities for several novel chemical reactions. These unique properties of zeolites have attracted much attention in scientific research to exploit them as hosts for catalytically active guest molecules. A wide variety of metal clusters, organometallic compounds and coordination compounds have been encapsulated in numerous zeolite hosts. Such catalysts have found several applications including size or shape selective catalysis, electro and photocatalysis and a variety of organic oxidation and hydrogenation reactions. These composite materials are believed to exhibit activity and selectivity comparable or enhanced to those of guest molecules.

1.5.1 Milestones

Much of the initial research work in the field of zeolite catalysis focused on the catalytic properties of zeolite itself. The crystalline network structure of zeolite attracted researchers interested in heterogenizing homogeneous catalysts. Initial goal was to produce metal clusters within zeolites X and Y. Various methods were used for the synthesis of metal clusters inside zeolite cavity, including decomposition of carbonyl clusters, impregnation with a solution of metal atom, reduction of ion exchanged transition metal cations, etc. In spite of having disadvantages such as migration of metal clusters to the external surface and subsequent agglomerisation, considerable success was achieved in producing highly dispersed metal particles inside the zeolite host.

Carbonyls form another class of compounds of interest for encapsulating in zeolites as their potential for catalytic applications is quite high. For example, Mo(CO)₆,
supported in Y zeolite modified with Li was reported to be particularly active for hydrogenation reactions 99. The intrazeolite chemistry of iron carbonyls also received much attention. Fe(CO)$_3$, Fe$_2$(CO)$_9$ and Fe$_3$(CO)$_{12}$ were adsorbed in Y-zeolite without any change in the structure 100. Zeolite X or Y supported dicobalt octacarbonyls were prepared by either direct sublimation 101 or adsorption from pentane solution 102. Nickel tetracarbonyl in zeolite support was also studied 103.

Zeolites, X and Y allow the entrapment of certain organometallics like bis(dithiophosphato)nickel which cannot be supported on carrier like silica gel 104. Tris(π-allyl)rhodium was a well studied system to illustrate the synthesis of organometallic compounds in zeolite cavities 105. Metalloccenes can be easily exchanged into zeolites and its interactions with zeolite lattice can be studied using various spectroscopic techniques. Goder and Ozin exchanged ferrocene and found its homogeneous distribution in zeolite 106. Zeolites were also used to preferentially support redox active species, both internally and externally. It is interesting that such systems allow rapid electron transfer between the surface species and intrazeolite species 107.

Many coordination complexes were prepared in zeolites not only with a view to derive active and selective catalysts but also to investigate the interactions between the zeolite framework and the complexes. The early work was confined to some systems that are not very stable and can be destroyed by evacuation or gentle heating 108-110. Intrazeolite hexamethylisocyanide complex of Co was one of such well characterized complex 111. Later, several workers focused on the encapsulation of complexes of monodentate ligands. These studies were first reviewed by Lungford 111, 112 and later on by Mortier and Schoonheydt 113 and Ozin and Gil 114. A few complexes with bi- and polydentate ligands were synthesized in zeolites and characterized. Among them, metal complexes of ethylenediamine, pyridine, salen, phthalocyanine and porphyrin have received much attraction as effective catalysts for various reactions 115-118.
1.5.2 Structural considerations

Zeolites are microporous, crystalline, three dimensional aluminosilicates composed of SiO$_4$ and AlO$_4^-$ tetrahedra joined through shared oxygen bridges. These tetrahedra are arranged in such a way that two Al atoms never come in the adjoining tetrahedra but are separated by at least one silicon tetrahedron. The basic building block of A, X and Y zeolite is a sodalite unit which is a cubo-octahedron formed from 24 tetrahedra of SiO$_4$ and AlO$_4^-$ and consists of six 4-membered cube faces and eight 6-membered octahedron faces. When the sodalite units are connected each other at their square faces, the resulting structure is called A-zeolite and if they are joined at the hexagonal faces, X and Y structures are formed. The large cavities in these zeolite structures are called super cage or $\alpha$-cage while smaller cavities are called sodalite cage or $\beta$-cage. The structure of Y zeolite is shown in Figure I. 1. The unit cell formulae and other characteristics of A, X and Y zeolites are given in Table I. 1.

Table I. 1
Properties of zeolites A, X and Y

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Unit cell formula</th>
<th>Mol. ratio SiO$_4$/Al$_2$O$_3$</th>
<th>$\alpha$-cage diameter</th>
<th>$\alpha$-cage aperture</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Na$_{12}$(AlO$<em>2$)$</em>{12}$ (SiO$<em>2$)$</em>{12}$ nH$_2$O</td>
<td>2 : 1</td>
<td>11 Å</td>
<td>4 Å</td>
</tr>
<tr>
<td>X</td>
<td>Na$_{86}$(AlO$<em>2$)$</em>{86}$(SiO$<em>2$)$</em>{106}$ nH$_2$O</td>
<td>2.5 : 1</td>
<td>13 Å</td>
<td>8 Å</td>
</tr>
<tr>
<td>Y</td>
<td>Na$_{56}$(AlO$<em>2$)$</em>{56}$(SiO$<em>2$)$</em>{136}$ nH$_2$O</td>
<td>5 : 1</td>
<td>13 Å</td>
<td>8 Å</td>
</tr>
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Silicon tetrahedron maintains electrical neutrality whereas a trivalent Al atom when bound to four oxygen atoms, the resultant Al tetrahedron will have a net negative charge. In synthetic zeolites, the net negative charge on the lattice is counter balanced by protons. It is also possible to introduce transition metal ions into the zeolite lattice in place of protons by ion exchanging Na$^+$ form of the zeolite with desired transition metal ion. The existence of exchangeable cations in the zeolite lattice provides the possibility of inclusion of metals and chemically interesting metal complexes.
Figure I. 1

(a). SiO$_4$ tetrahedra, (b). AlO$_4$ tetrahedral, (c). Sodalite unit

(d). Y Zeolite and (e). Y Zeolite encapsulated iron phthalocyanine
Metal complexes of about 10 to 13 Å in diameter can be synthesized inside the α-cage of zeolites X and Y. As the openings of the cages are small, the complexes once formed inside the cages cannot move out through the openings, but remain trapped. Zeolite can be considered as a solid solvent and the entrapped molecule as a solute which is not mobile. During catalysis, zeolite cage acts as a molecular scale microreactor containing metal complex catalyst. The reactants can enter through openings, undergo reaction at metal site and exit as products. In this special microreactor, the framework atoms (reactor walls) also influence the catalytic activity through its electronic and steric effects on the encapsulated complexes. Additionally, the well known sieving and orienting properties of zeolite network structure could be explored in catalytic reactions which require high selectivity.

1.5.3 Merits and Demerits

Synthesis of metal complexes in the super cage of zeolites offers several advantages over their homogeneous counterparts so as to conveniently use them as catalysts for many reactions. It is generally stated that the activity of metal complex in solution phase is retained or improved on encapsulating in zeolite cavities. In addition, the encapsulated complexes are able to work at milder temperature and pressure as compared to that of conventional heterogeneous catalysts. The most attractive advantage of such heterogenized systems is the ease of separation of catalysts from reactants and products. In fact, zeolite encapsulated metal complexes combine the merits of both homogeneous and heterogeneous catalytic systems, but at the same time, minimise the demerits of both.

Zeolites are attractive hosts for catalytic species due to their high thermal stability, well defined structure, large internal surface area, etc. Enhanced size and shape selectivity due to zeolite framework besides that due to the constraints in guest molecule is an important feature of encapsulated catalysts. The interaction of metal complex with zeolite may alter its electronic structure and thereby its catalytic performance. In short,
besides the tremendous activity of guest compounds, the encapsulated catalysts show
the attractive features of zeolites.

The stability of metal complexes in actual reaction conditions is expected to be
improved on encapsulating in zeolite pores \(^\text{121}\). This effect may be explained in terms of
the following aspects: (1) the complexes are immobilized inside the cavity, (2)
dimerisation processes of the complexes are retarded resulting longer life and (3) zeolite
imparts additional stability to the complex by acting as ligands. The high stability of the
catalysts provides the ability to work at elevated temperatures which in turn tend to
overcome diffusional restrictions, promote reactions with high activation energy and to
withstand severe conditions of regeneration process.

Like any other catalytic material zeolite encapsulated metal complexes also have
some limitations \(^\text{114}\). The various problems associated with zeolite catalysts including
pore plugging, poisoning, migration, leaching and structural defects of zeolite matrix are
also applicable in the case of catalysts immobilized in them. The catalytic activity may be
severely affected by clogging of pores by products. Such situations make necessary
frequent catalyst regeneration by high temperature operation that is difficult when
encapsulated complex is thermally unstable. Less mobility of molecules in zeolite cavity
due to the entrapped complexes restricts its use for catalysing reactions of bigger
molecules. However, the main issue in encapsulation is the preparation of
homogeneously distributed metal complexes in zeolite framework. The goal of achieving
well defined intrazeolite catalysts is possible only by strictly optimising the preparation
conditions.

1.5.4 Enzymes and Enzyme mimics

Enzymes are one of the most efficient catalysts known which exhibit extreme
selectivities in chemical transformations. Enzymes catalyse reactions at ambient
temperatures, that are possible on heterogeneous systems only at high temperatures and
pressures. It is also interesting to mention that they are environment friendly catalysts
working without producing any hazardous by-products. A large number of drugs, pharmaceuticals and specialty chemicals are manufactured by biochemical methods using enzymes. In spite of the remarkable achievements in biocatalysis, enzyme technology has limited to the low volume, high value chemicals due to raw material wastage in cell growth, difficulties in product separation, non-continuous operation and low stability of biochemical catalysts.

Enzymes are composed of a metal complex as active site embedded in a large protein structure. The functions of protein molecule are: (1) protecting active sites from self destructing reactions like dimerisation; (2) inducing substrate selectivity due to protein channels; and (3) providing stereochemical environment at the active centre for the specific chemical transformation to take place. The desire to understand and exploit the chemistry of enzymes has prompted an extensive research on synthetic porphyrin, phthalocyanine and Schiff base models of enzyme active sites and later on superstructured mimics with a controlled steric environment for better selectivity. The comparative evaluation of activity, selectivity and stability of both synthetic models and natural enzymes has given very promising results in the case of biomimetic oxidation of hydrocarbons.

It was known that inorganic materials like zeolite could provide the best arrangement for the catalytically active sites in their cavities and direct substrates towards it. Furthermore, the channels and cages in zeolite framework are very similar to those created by the protein structure of enzyme. Hence, new catalysts can be designed by replacing the protein portion of natural enzymes by the zeolite framework. These hybrid catalysts combine the attractive features of zeolites and tremendous activity and selectivity of enzymes. Therefore, zeolite encapsulated metal complexes, referred to as "Zeozymes", have been described as model compounds for mimicking enzymes.

Several zeolite complexes were designed and successfully developed to act as zeozymes with respect to activity and stability in catalytic reactions. Nature performs
selective oxidation of organic materials to usable hydrophilic compounds by means of the monooxygenase enzymes of the cytochrome P450 family. The desire to mimic cytochrome P450 has led to the development of new zeolite based Fe/Pd oxidation catalysts. Models of cytochrome P450 consisting of organometallic complexes encapsulated in zeolites were also designed. These systems control selectivity and inhibit autoxidation, but do not show any mechanistic analogy with enzymatic processes and exhibit only low oxidation rate as compared to that of enzymes.

Recently, an efficient mimic for cytochrome P450 was reported and its catalytic activity was found to be promising for industrial applications. This catalyst comprises iron phthalocyanine (FePc) complexes encapsulated in Y zeolite which are in turn embedded in a polydimethylsiloxane (PDMS) membrane as represented in Figure 1.2. The role of polymer is to act as an interface between two immiscible phases as phospholipid membrane in which cytochrome P450 resides. This system oxidises alkanes at room temperature at rates comparable to those of the enzyme. Furthermore, the oxidation activity of zeolite encapsulated iron phthalocyanine complex has enhanced to 300 times higher on supporting in the membrane. Intrazeolite complex preferentially sorbs polar compounds, whereas membrane embedded system sorbs cyclohexane and creates a barrier against polar compounds. Moreover, the polymer allows high sorption and fast diffusion of reagents together with the homogeneous distribution of catalyst particles.

Zeolite encapsulated cobalt(I) salen was also suggested as a synthetic mimic for studying the oxygen binding properties of hemoglobin. A cross sectional representation of this system is shown in Figure 1.3. This system is superior to other reported models with respect to the stability against deteriorous processes of autoxidation and dimerisation. However, in contrary to the behaviour of hemoglobin, the rate of oxygen binding decreases after the initial adsorption. This may be due to the fact that the binding becomes increasingly difficult as the molecule moves from the exterior to interior of zeolite crystallite.
Figure 1. 2
Schematic representation of encapsulation of FePc and subsequent incorporation in PDMS-membrane

Figure 1. 3
Cross sectional representation of Cobalt(I) salen
1.6  **ZEOLITE ENCAPSULATION METHODS**

Three methods, currently used for encapsulating metal complexes in zeolites are:

1) **Flexible ligand method** involves diffusion of ligand molecules through the zeolite pores followed by reaction with transition metal ions previously introduced into the lattice.

2) **Ship-in-the bottle method** - the metal complex is synthesized inside the zeolite cavity from smaller components or assembling the ligand from smaller species around the transition metal ions inside the zeolite cavities.

3) **Zeolite synthesis method** - involves the synthesis of zeolite structure around the pre-formed transition metal complex.

These three approaches are discussed below:

1.6.1  **Flexible ligand method**

In this approach the ligand molecule must be flexible enough to diffuse through the zeolite pores. Once the ligand has entered the zeolite cage and reacted with previously exchanged transition metal ions, the complex formed is too large and rigid, and therefore it cannot escape from the cages.

This concept was first experimented by Herron \(^{137}\) to prepare Co-salen complexes in the supercages of faujacite. The salen ligand offers a high desired flexibility to pass through the zeolite channels due to the possible free rotation around the C-C σ-bond connecting the two salicylidene moieties. This has led to the synthesis of salen complexes with cobalt \(^{137}\), manganese \(^{119}\), iron \(^{138}\), rhodium \(^{139}\) and palladium \(^{140}\) ions within Y-zeolite cages. This method was used for preparing complexes of several simple ligands like bipyridine. Highly selective complexation of these ligands to form bis- or tris- coordinated complex in zeolite cavities was achieved by adjusting the ligand to metal ion ratio and the temperature of synthesis \(^{141,142}\). Later on, transition metal complexes of several other Schiff base ligands were encapsulated \(^{119,143}\).
1.6.2 Ship-in-a-Bottle method

Ship-in-a-Bottle method was first used by Romanovsky and co-workers. Later, phthalocyanine complexes of cobalt, copper, iron, manganese, nickel, osmium, rhodium, and ruthenium were synthesized. This method involves the diffusion of dicyanobenzenes into the zeolite matrix where it undergoes cyclisation around a previously introduced metal ion to form a tetradendate macrocycle which is too large to exit. After mixing the ion exchanged zeolite and 1,2-dicyanobenzenes, tetramerisation is induced by heating in vacuum at temperatures between 250 °C and 350 °C. The complexation temperature determined by differential scanning calorimetry varies with the type of transition metal ion and the structure of the zeolite. The reaction takes place according to Eq. 1.1.

\[ \text{M}^{2+} + 4\text{DCBz} + \text{H}_2\text{O} \rightarrow \text{MPCY} + 1/2\text{O}_2 + 2\text{H}^+ \]  

Eq. 1.1

Zeolite encapsulated substituted phthalocyanines were synthesized by using substituted dicyanobenzenes as starting reagent. For example, the synthesis of intrazeolite tetra-t-butyl-substituted iron-phthalocyanine, perfluorophthalocyanines of iron, cobalt, copper, and manganese and iron-tetranitrophthalocyanine was reported. However, in the case of tetranitrophthalocyanines, it was doubtful that the complexes are located mostly on the external surface.

Another approach of Ship-in-a-Bottle synthesis involves the introduction of the transition metal by adsorption of corresponding carbonyl complex or metallocene in zeolite, followed by the synthesis of phthalocyanine ligand around the transition metal. This method was mainly used for preparing intrazeolite iron-phthalocyanine from the adsorbed iron pentacarbonyls or ferrocene. Intrazeolite iron pentacarbonyls are decomposed thermally leading to metal clusters in the supercages which react with dicyanobenzene to give metal phthalocyanine. Alternatively, metal carbonyls can also be introduced by direct ligand exchange of CO by 1,2-dicyanobenzene at lower temperatures. As indicated in Eq. 1.2, no protons and hence no acid sites are produced.
during complex formation via carbonyl route. However, in both cases the major disadvantage is the formation of large amount of excess metal clusters in zeolite since only one phthalocyanine complex can be formed per super cage.

\[
\text{M(CO)ₙ} + \text{Y} + 4\text{DCBz} \rightarrow \text{MPcY} + n\text{CO}
\]  
Eq. I. 2

The use of adsorbed ferrocene as a source for iron was also successfully described by Parton et al.\(^\text{158}\). This reaction is represented in Eq. I. 3.

\[
\text{M(Cp)₂} + \text{Y} + 4\text{DCBz} + \text{H₂O} \rightarrow \text{MPcY} + 2\text{Cpen} + 1/2\text{O₂}
\]  
Eq. I. 3

This method has the advantage that the encapsulated complex is free from uncomplexed metal species. However, large amount of free phthalocyanine was observed inside the zeolite after complexation reaction.\(^\text{159}\). The entrapped free ligands may create diffusional restrictions in pores for reactants and products in various catalytic reactions.

Ship-in-a-Bottle technique was also applied for encapsulating complexes in molecular sieves without cation exchange capacity, such as VPI-5\(^\text{158}\) and for the synthesis of porphyrin type ligands in the super cages of Y-zeolite. The encapsulation of iron and manganese-tetramethylporphyrin in the super cages of Y-zeolite was reported by Nakamura et al.\(^\text{160}\). Chan and Wilson\(^\text{161}\) claimed the formation of intrazeolite tetraphenylporphyrins on treating metal exchanged zeolite with pyrrol and benzaldehyde.\(^\text{161}\) However, more experimental evidences yet to be presented for ensuring true complex encapsulation.

1.6.3 Zeolite synthesis method

Zeolite synthesis method is a recent innovation in which metal complexes are encapsulated by forming zeolite structure around the preformed complexes.\(^\text{162-165}\) The complex is added as a template during the crystallisation of zeolites. This method can be applied only if the complex is stable enough to withstand the zeolite synthesis
conditions (i.e., pH, temperature and hydrothermal condition) and has sufficient solubility to get a random distribution of the complex in the synthesis medium to form well defined homogeneous product. This method offers several advantages including mild preparation conditions and well defined intrazeolite metal complexes.

Rankel and Valyocsik\textsuperscript{162} attempted the synthesis of intrazeolite complexes of bipyridine, phenanthroline and phthalocyanine by this method. It was claimed that the homogeneous encapsulation of metal complexes is possible in zeolite X and, AlPO\textsubscript{4}-5 and AlPO\textsubscript{4}-11 by preventing the aggregation of the complexes in aqueous synthesis medium. If organic templates are used for zeolite synthesis, they are removed by calcining the final product. The intrazeolite complex might be destroyed during this calcination step. Hence, zeolite synthesis method appears to be effective only in the cases where the synthesis of zeolite matrix is possible without the use of any further organic templates.

1.7 CHARACTERISATION OF ZEOLITE COMPLEXES

Encapsulation of metal complexes in porous solids like zeolite helps to combine the characteristics of both zeolite and metal complex to obtain new hybrid catalysts. A complete characterization of such composite materials is necessary to ensure encapsulation and provide fruitful informations on the real state of complex and zeolite support. In general, zeolite encapsulated complexes are characterized to address the following aspects:

1. internal versus external confinement and the distribution of guest compounds in zeolite host
2. nature of the complex formed in zeolite cavity compared to that in solution phase
3. the degree of complexation
4. the effect of host-guest interactions on the structure of complex.
5. whether zeolite framework is preserved on encapsulation

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6. the stability in comparison to free metal complexes
7. the ability to provide vacant coordination sites for catalytic reaction.

Several approaches have been reported for investigating above aspects and their influence on catalytic performance. These approaches include molecular modelling, entrapment identification, physico-chemical properties of the zeolite complexes, adsorption studies, stability studies and electrochemical studies. A brief account of various characterization methods is given below:

1.7.1 Molecular modelling and simulation

The use of computerised molecular graphics analysis has provided a better understanding of the properties of zeolite encapsulated complexes and the science behind their catalysis. The structure of Y zeolite encapsulated iron phthalocyanine (FePc) has been studied using molecular modelling method. It was shown that the FePc was located at the center of the supercage with the bridging N atoms pointing towards the four rings of the cubo-octahedra. The planarity of the complex is disturbed to accommodate bigger phthalocyanine ligand in the supercage.

Molecular graphics techniques are also useful for modelling and simulating catalysis in zeolite cavities, particularly for studying the selectivity of zeolite based catalysts. The computer simulation can be achieved either by energy minimization method or by molecular dynamics method. In the first approach, the system moves towards a potential energy minimum through a low energy pathway, whereas the latter approach allows the simulation of a complete chemical system at a finite temperature and pressure in which properties are evolved as a function of time.

1.7.2 Entrapment identification

The main issue in the synthesis of zeolite encapsulated complexes is to recognize appropriate conditions at which well defined distribution of guest compounds occur in the zeolite cage, instead of being concentrated on the external surface. The distribution
of guest compounds in zeolite host can be ascertained by several chemical methods. One of such methods is size-dependent chemical reaction as illustrated by reactions between phosphines and encapsulated metal carbonyls. With smaller phosphines, all the supported carbonyls react to form anionic species in zeolite lattice, but no reaction is observed with phosphines too large to penetrate the pore openings of the zeolite.

The internal entrapment can also be confirmed by studying size/shape selectivity which is imparted by the molecular discriminating nature of the zeolite lattice. For example, Mo(CO)_6 in alkali metal exchanged Y zeolite has showed high activity and selectivity in the hydrogenation of 1,3-butadiene whereas nonzeolitic supports exhibited nonselective hydrogenation properties. Similarly, zeolite encapsulated Rh(allyl)_2 exhibits high selectivity in olefin hydrogenation as compared to silica supported analogue. To establish the internal confinement of this species, catalytic self poisoning reactions have also been carried out with phosphines of varying sizes. Only smaller phosphines which can penetrate zeolite pores are able to reduce the catalytic activity by coordinating with the entrapped complexes.

In another method, zeolite framework is destroyed by treating with Con. H_2SO_4 and the resulting solution is analysed by UV-Vis. spectroscopy for directly detecting metal complex previously encapsulated in the framework. However, this method can be used only if the complex is stable in Con H_2SO_4.

Besides such chemical methods, modern physical techniques are also used to ensure the presence of guest molecules in zeolite cavities. Some of these techniques are discussed in next section.

1.7.3 Physico-chemical methods

(a) Chemical analysis

Chemical analysis is used to find the composition of zeolite complexes. The degree of ion exchange in zeolite and the unit cell formula are derived from the analytical
data. The Si/Al ratio of the zeolite complexes is compared with that of pure zeolite to make sure that zeolite framework is preserved on encapsulating complexes.

(b). **CHN analysis**

CHN analysis is performed to quantify organic ligands complexed to the metal ions. These analytical data also provide informations on the extent of complexation and help to identify the presence of uncomplexed metal ions which are not removed on ion exchanging at the final stage of synthesis.

(c). **Surface area analysis**

Surface area measurement is the easiest probe to detect encapsulation of guest molecules in zeolite cavities. A lower surface area of intrazeolite complex as compared to metal exchanged zeolite indicates the filling of zeolite pores with complexes. Usually, BET surface area is measured by nitrogen adsorption at liquid nitrogen temperature.

(d). **X-ray diffraction spectroscopy**

X-ray diffraction is used to study the diffraction pattern of the zeolite. The evaluation of the spectra of host zeolite and zeolite complex is carried out to ensure that zeolite crystallinity is not affected by the encapsulation of metal complex.

(e). **Electronic spectroscopy**

The ultraviolet and visible light absorption spectroscopy gives information about the d orbital splitting of metal ions and ligand-metal interactions through the ligand to metal charge transfer transitions. The nature of coordination can be studied by comparing the spectra with those of known complexes. For example, diffuse reflectance spectroscopy has been applied to tris(ethylenediamine) complex of Co(II) in zeolite Y. The appearance of a band at 20650 cm\(^{-1}\), characteristic d-d transition of an octahedral complex, indicates chelate formation. This complex is stable upto 200 °C, but it
decomposes at higher temperatures to monoligand complex which arises charge transfer bands in the UV region.

Interestingly, the process of formation of dimethylglyoximato-Co(II) complex during the uptake of dimethylglyoxime in Co-X zeolite has been monitored by in situ UV/Vis microscope spectrophotometry. In the case of zeolite entrapped cobalt phthalocyanine complexes, UV-Vis spectra exhibit a splitting of the Q band, which is expected for a lowering of symmetry from $D_{4h}$ to $D_{2h}$. The protons formed during the complex formation cause partial protonation of the encapsulated metal phthalocyanine and hence symmetry is lowered to $D_{2h}$. Furthermore, luminescence spectra in UV-Vis region provide informations about the distribution of complexes in the zeolite lattice.

(f). **Fourier Transform Infrared spectroscopy**

FTIR spectroscopy provides valuable evidences for the formation of metal complexes in zeolite pores. The ligand molecules are coordinated to transition metal cations if different spectral patterns appear in the free and chelated state or if characteristic bands exhibit shift in frequency upon coordination.

(g). **EPR spectroscopy**

EPR spectroscopy is a powerful probe to study the bonding of metal complexes in zeolite cavity. For example, it was used to investigate the square planar complexes of Co(II) with low spin ($S=1/2$) doublet ground state in which $3d^6$ orbital occupies the unpaired electron. The spin Hamiltonian parameters of such ground states undergo changes during axial ligation which provides means to study the processes of complexation. The complexation process in tetrakis(pyridine)copper(II) was studied much clearly by evaluating the intensity changes in EPR spectra. Tris(bipyridine) complexes of Co(II), Fe(III) and Ru(III) in Y zeolite are stable in low spin state upto $-196 \, ^\circ C$, above which the formation of a high spin octahedral state is identified by EPR spectra. EPR spectra are also useful to distinguish monomeric and dimeric complexes from the multiplicity of the hyperfine structure. Zeolite entrapped
Co(II)-Schiff base complexes were analysed for EPR spectra with a view to study the influences of zeolite host on the geometry of the complex. In zeolite encapsulated cobalt phthalocyanines, the protons released during complexation interact with the nitrogen atoms of the complex, resulting non-equivalency of nitrogen atoms which could also be identified by EPR spectra.

(h). **Conventional Transmission Electron Microscopy**

The size and shape of solid particles, higher than 100 nm can be measured by conventional transmission electron microscopy.

(i). **High Resolution Electron Microscopy**

The measurement particle size below the nanoscale of individual unit cells is performed by high resolution electron microscopy. This technique is useful to study the formation of extra material on or inside the zeolites and to detect any change in the zeolite framework on encapsulating metal complexes.

(j). **X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy can be applied to determine the chemical composition of external parts of the solid in a few nanometers in depth as well as to study the chemical state of surface atoms. The XPS data of encapsulated complexes provide following informations:

1. the distribution of encapsulated complexes in zeolite lattice i.e. either homogeneously distributed throughout the lattice or enriched in a shell close to the zeolite surface.
2. the degree of complexation
3. the structure of complex
4. the interaction with the framework \(^{183-185}\)
From the detailed analysis of surface elements, it is possible to detect preferential location of metal complex by comparing M:Si, M:Na and L:Si (L is a ligand element) with those expected for bulk composition. A deviation of these values to higher side indicates enrichment of species at or close to the external surface of zeolite lattice. In the case of nickel phthalocyanine encapsulated in Y zeolite, for example, the extent of binding of metal ions to phthalocyanine ligand can be determined via N:Ni ratio. The degree of complexation increases as this ratio approaches the maximum value of 8. The reduction of binding energy of the metal from 855.8 for NiY to 854.9 for NiPcY is also an interesting proof for high degree complex formation. The structure of zeolite encapsulated metal phthalocyanine can strongly deviate from that of the free complex. This is indicated by a change of XPS spectra as in the case of NiPcY which gives a doublet instead of a singlet for free complex.

(k). NMR spectroscopy

High resolution magic angle spinning nuclear magnetic resonance spectroscopy (HR MAS NMR) is used to study the interaction of phthalocyanines with the zeolite framework. This study has shown the existence of strong interaction between Al atoms in the pore walls and hydrogen atoms of the phthalocyanine molecule. As a result of these interactions, zeolite framework undergoes local deformations which are indicated by the loss of resolution in the spectrum.

1.7.4 Oxygen adsorption

Oxygen adsorption is used to determine the fraction of complexed metal ions in the zeolite lattice which are capable to bind oxygen molecules. The oxygen pulse technique has been applied to measure this fraction of Co(II) metal ions in [Co(II)(bipyridine)(terpyridine)]$^{2+}$-LiY zeolite. By this technique, it would be possible to identify the metal complexes which are able to take up oxygen reversibly or irreversibly. For example, cobalt complex of bis(salicylidine)ethylenediamine in zeolite Y does not allow the reversible uptake of oxygen, but it is possible with cobalt complexes
of bis(salicylaldehyde)-methyldipropyltriamine in zeolite NaY. The adsorption of oxygen on the metal sites is controlled by the diffusion process.

1.7.5 Thermal analysis

The thermal stability of zeolite encapsulated complexes can be studied by thermogravimetric analysis. Thermal analysis of intrazeolite metal phthalocyanines has been performed in air, oxygen, hydrogen and helium. The complexes are stable up to 873 K in helium, but decompose at a faster rate in air and hydrogen at 700 K and even below at < 500 K in oxygen. The poor stability of the encapsulated complex in oxygen atmosphere has been reflected in both gas phase and liquid phase oxidation reactions with molecular oxygen. However, zeolite complexes are not significantly affected in oxyfunctionalisation reactions of alkanes or alkenes at room temperature using t-butylhydroperoxide or iodosobenzene. Also, in the case of metal-porphyrin compounds, photostability has been enhanced upon encapsulating in zeolites.

1.7.6 Electrochemical methods

Increased interest in the encapsulation of metal complexes in supercages of zeolites has prompted several workers to study the electrochemical behavior of various zeolite entrapped complexes and thereby assess the possibility of using them in electrocatalysis. It is known that electrochemical technique such as cyclic voltammetry provides information on the oxidation state and redox chemistry of the active metal atom. This technique also gives means to recognize the location of guest compounds i.e. at the external surface or encapsulated in zeolite pores. The mechanism of electron transfer was suggested by Shaw et al. for electroactive ion exchanged zeolite and zeolite encapsulated complexes. In the former case, electron transfer takes place after the electroactive species is exchanged out of the zeolite by electrolyte cations whereas the latter undergo electron transfer within the zeolite cavities.

The electrochemistry of zeolite encapsulated phthalocyanine complexes was extensively studied. Encapsulated perhalogenated phthalocyanines also show well
defined redox behavior which is difficult to observe in solution phase. Ni(bpy) encapsulated in Y zeolite was used for the electroassisted catalytic reduction of organic halides like benzyl chloride, but large molecule like triphenylmethyl bromide is unreactive. It is expected that this electrochemical behavior reflects the activity and selectivity of intrazeolite complexes. The electroactivity of encapsulated Mn(III)-salen and Ru(III)-salen is very similar to that of dissolved complexes in solution. In the case of encapsulated Co(II)-salen and Fe(III)-salen, the existence of two redox processes indicates the existence of two metal-salen structures in zeolite cavity. These structures are identified as planar or nonplanar tetradentate structure and bidentate structures. These results indicate that zeolite may be involved in the coordination of the metal ions.

1.8 HOST-GUEST INTERACTIONS IN ZEOLITE COMPLEXES

A better understanding of the influence of zeolite architecture on the structure and reactivity of encapsulated guest complexes is expected to facilitate the design of active catalysts for various chemical reactions. A combination of various spectral techniques is used to study the host-guest interactions in zeolite encapsulated complexes. Herron et al. reported the changes in the properties of tetracarbonyl nickel as a result of encapsulation in zeolite X. It appears that zeolite allows the formation of highly reactive, moderately long lived, coordinatively unsaturated Ni(CO)₄ species in the cavities, whereas no such reactive species can exist in solution phase.

The electrostatic interaction between the zeolite framework and the metal complex is considerably important for understanding the role of zeolite support in the catalysis by encapsulated complexes. For example, copper-amine complex, an intermediate in the catalytic oxidation of ammonia, was encapsulated and studied by Raman spectroscopy. Pronounced electrostatic interactions have been seen in the absence of water in the zeolite lattice.
Tris(bipyridine)ruthenium(I) in zeolite Y was prepared for investigating the host-guest interactions as they are highly probable in such systems to the close proximity of the periphery of the bipyridine ligand to the anionic zeolite framework. The excited state properties of Ru(bpy)$_2^+$ are influenced by zeolite framework upon dehydration, whereas ground state structure is not perturbed. However, this complex in hydrated zeolite resembles its aqueous solution. Tiwary and Vasudevan have also reported the effect of zeolite topology on the geometry of this encapsulated complex. Comparative spectroscopic, magnetic and molecular graphics investigations of free and encapsulated complex indicated that encapsulation partially reduces the triagonal distortion observed in unencapsulated complex to restore octahedral geometry. Zeolite encapsulated tris(2,2'-bipyridine)iron was also investigated for the interactions of zeolite framework which induce unusual chemical and physical behaviour for the encapsulated complex.

The difference in the behaviour of Schiff base complexes of Co(II) formed in solution and that in a zeolite cage was studied by changing the polydentate Schiff base ligands. With tetradentate ligand such as salen, four coordinate low spin Co(II) complexes are formed only in low yield in zeolite Y. But in solutions, Shiff base usually readily reacts with the metal to form complexes. However, pentadentate ligands are more effective in reacting with Co(II) ions in zeolite to form complexes in the pores. These observations also reflect the influence of zeolite matrix on complex formation.

1.9 CATALYSIS BY ZEOLITE ENCAPSULATED COMPLEXES

Zeolite encapsulated metal complexes provide reaction centres for binding and catalysis of molecules those are mobile in zeolite pores. The steric constraints in zeolite may distort the encapsulated molecules to induce different stability and reactivity for them. The presence of ligand molecules coordinated to the metal enhances the selectivity of metal exchanged zeolites in catalytic reactions. Thus, zeolite encapsulated complexes have catalytic properties which are different from those of cation exchanged zeolite and virgin metal complex. Interestingly, the activity, selectivity and stability of
zeolite complexes are found to be very promising to be exploited as catalysts in various industrially important reactions.

Early investigations on the catalysis by intrazeolite species include the use of zeolite X or Y entrapped metal carbonyls for water gas shift reaction, carbonylation of methanol and aromatic compounds and hydroformylation. For example, Mo(CO)$_6$/M$^+$Y (M = Li, Na, K, Cs) was reported to be highly active and selective in the hydrogenation of 1,3-butadiene to cis-2-butene. Zeolite encapsulated monovalent carbonyl species, M-(CO)$_2$$^+$, of iridium and rhodium are active catalysts for carbonylation of methanol in the presence of methyl iodide and the water gas shift reaction. However, [Rh(CO)$_2$Cl]$_2$ in Na-Y appears to be inferior to that supported on alumina with respect to the activity for water gas shift reaction. [Pt$_{15}$(CO)$_{30}$]$^+$ was synthesized in FSM-16 (folded-sheet mesoporous material) and was found to be very effective for water gas shift reaction. The high activity of this system might be due to the high diffusibility of reactant gases in the honeycomb structure with ordered enormous channels of 20-100 Å diameters. Fe$_3$(CO)$_{12}$ in zeolite was also attracted attention as an excellent catalyst for the conversion of syngas.

The catalytic properties of zeolite encapsulated metal complexes have been extensively explored in various oxidation reactions. They include the oxidation of carbon monoxide, oxidative coupling of methane to methanol over ruthenium-, cobalt-, or manganese-phthalocyanines, oxidation of linear and cyclic alkanes, oxidation of hydroquinone to benzoquinone, oxidation of ethylbenzene, oxidation of mercaptanes to disulfides, etc. Many different oxidising agents were used in homogeneously catalysed oxidation reactions. However, in the case of zeolite complexes only a few of the oxidants can be used due to one or more of the following disadvantages.

1. oxidants like aromatic peracids are too large to diffuse through the zeolite pores.
2. oxidants like NaClO require a phase transfer catalyst which is too bulky to enter the pores.

3. they are highly expensive.

4. they are not acceptable under environmental aspects.

Generally oxidants like iodosobenzene, organic peroxides, hydrogen peroxide and molecular oxygen are used for oxidation reactions on zeolite complexes. Iodosobenzene (PhIO) was particularly attractive in homogeneous catalysis as oxygen atom donor since it does not form radicals. Also, PhIO can be easily separated from the reaction products as it is insoluble in solvents like acetonitrile. In addition, direct measurement of oxygen transferred to reactants is possible by quantitatively analysing the PhI formed during the reaction. But it has certain disadvantages in oxidation reactions over zeolite catalysts. The two main demerits are reduced reaction rates due to its relatively low mobility in the zeolite pores and the formation of iodoxybenzene by disproportionation of iodosobenzene. The former causes iodosobenzene molecules to be trapped in the pores leading to deactivation of the catalyst by pore blocking. Organic peroxides like t-butylhydrogen peroxide are better oxidising agents than iodosobenzene for zeolite catalysts. However, the amount of uncomplexed metal ions in the zeolite should be minimized to avoid the decomposition of peroxides.

The catalytic properties of encapsulated copper phthalocyanines for the oxidation of methane, phenol and aliphatic and aromatic hydrocarbons have been described. Cobalt phthalocyanine in faujasite X is able to oxidise propene with high selectivity and resistant to rapid deactivation. Zeolite X or Y encapsulated iron phthalocyanine complex catalyses the oxidation of alkanes to alcohols and ketones under ambient conditions with iodosobenzene or t-butylhydrogen peroxide. The catalytic activity of Y zeolite encapsulated iron phthalocyanine complex for the oxidation of a series of homologous n-alkanes was compared with that of free iron phthalocyanine. It was observed that zeolite complex is much superior to free iron phthalocyanine with respect to oxidation efficiency. Moreover, whereas the free complex was completely deactivated during reaction, zeolite complex was found to be unaffected.
The sieving and orienting effect of zeolite framework to obtain high selectivity was also illustrated using phthalocyanine catalyst for the oxidation of alkanes. Zeolite entrapped iron phthalocyanine catalysts showed substrate selectivity, a preference for the smaller cyclohexane molecules in the oxidation of a cyclohexane/cyclododecane mixture with iodosobenzene. In contrast to this, the bulkier reactant, cyclododecane was oxidised three times faster than cyclohexane over free iron phthalocyanine. The preferential oxidation of smaller substrates on zeolite complexes can be enhanced by exchanging the zeolites with cations of increased size so as to reduce the effective pore width.

Regioselectivity was exemplified using this system. The oxidation of n-octane over free iron phthalocyanine occurs with equal selectivity at 2-, 3-, and 4- positions. Encapsulation of the complex in Y or in the molecular sieve VPI-5 results preferential oxidation at 2-position. This is attributed to the orienting effect of zeolite structure on reactant with respect to active sites so that oxidation at the end of chain is preferred. This effect is more pronounced in the case of Y-zeolite with smaller window size as compared to the VPI-5 structure with larger openings.

Herron reported stereoselective oxidations of methylcyclohexane and norbornane over zeolite encapsulated iron phthalocyanine complex. In the case of oxidation of methylcyclohexane to 4-methylcyclohexanol, the ratio of trans to cis isomers increases from 1.1 over free complex to 2, on encapsulation. In the oxidation of norbornane to norbornenol, encapsulation decreases the exo:endo ratio from 9.2 to 5.5. Stereoselectivity was also reported in the epoxidation of stilbene. Trans-stilbene is preferentially epoxidised over zeolite based iron phthalocyanine and t-butylphthalocyanine complex catalysts, whereas corresponding homogeneous complexes catalyse epoxidation of cis-stilbene more easily.

Zeolite encapsulated salen complex also received much attraction as efficient catalysts for the oxidation of organic compounds. Bowers and Dutta investigated the oxidation of cyclohexene, styrene and trans- and cis- stilbene over zeolite entrapped
manganese(III) salen complex. The rate of reaction is slower on the zeolite system as compared to that on corresponding homogeneous system. This may be due to the diffusional restrictions imposed by zeolite pores to prevent the substrate molecules from reaching the active sites located inside the supercage of zeolites. However, zeolite complex provides substrate selectivity based on size of the olefins and their mobility in zeolite pores.

Manganese (III) complexes of chloro- or bromo- substituted salen in Y zeolite are also known to catalyse aerobic oxidation of styrene. Improved product selectivity, catalyst life and catalyst recovery were observed in the case of zeolite encapsulated complexes than the corresponding homogeneous catalyst. Similarly, VO(salen)/Y was found to be active in the oxidation of toluene. Cu(II) salen/Y allows the oxidation of cyclohexanol to cyclohexanone at a temperature of 80 °C, whereas the commercial Cu based catalyst operates at 300 °C. Zeolite X or Y encapsulated halo- or nitro-substituted salen was evaluated for catalytic activity in the selective oxidation of some organic substrates. Encapsulated substituted salen complexes also exhibit promising performance in selective oxidation reaction and behave quite differently from both free complexes and Cu(II) exchanged zeolites.

Zeolite encapsulated Mn(II)-bipyridyl complexes are known to catalyse oxidation of various alkenes at room temperature. This supported complex avoids the problems like self oxidation encountered by their homogeneous counterparts and remains effective even after several cycles for cyclohexene oxidation with H₂O₂. Also, this system allows repeated regenerations without the loss of catalytic activity and spectroscopic properties of the complex. Another attractive catalyst is Cu(II)-pyrazole complex in zeolite X which is used for the oxidation of ascorbic acid.

Besides oxidation reactions, zeolite encapsulated complexes can also catalyse various hydrogenation reactions. The palladium(II)-salen complex catalyses the hydrogenation of alkene with poor substrate selectivity. In an attempt to improve the selectivity, Pd(II)-salen complex was encapsulated in zeolite X and Y.
The selectivity of this system was evaluated in the hydrogenation of equimolar mixture of hexene-1 and cyclohexene. The linear alkene is preferentially hydrogenated over the encapsulated catalyst, whereas both reactants are hydrogenated in the homogeneous hydrogenation using free Pd-salen. Also, the zeolite system offers advantages including no leaching of Pd as its complexes are trapped in zeolite cavity and hence reactions associated with the reduction of Pd(II) ion are not observed. Similar selectivity was also reported for Ni-salen entrapped in Y zeolite for the hydrogenation of hexene-1 in presence of cyclohexene. Kimura et al synthesized an electron donor-acceptor complex (Na+)4(FePc)4− in NaY by reacting FePcY with sodium naphthalene, Na+(C10H8). This complex showed an unusual selectivity to obtain high trans:cis ratio of butene-2 in the hydrogenation of butadiene.

Several industrially applied reactions have been studied on zeolite encapsulated transition metal complex catalysts. Direct synthesis of adipic acid from cyclohexane or cyclohexene, an industrially important process, can be catalysed by intrazeolite metal complexes. Zeolite Y supported iron-phthalocyanine and cis-manganese(II) bis-2,2'-bipyridyl are the two known zeolite complex catalysts for this application. The catalytic oxidation of cyclohexene with aqueous hydrogen peroxide gives cyclohexene oxime as the primary product which is converted to 1,2-cyclohexanediol by hydration. The latter is oxidised to 1,2-cyclohexanedione and adipic acid. The selectivity for adipic acid could be increased to 80% by optimising the catalyst and reaction conditions. However, the reaction rate is too low to replace existing commercial catalysts.

The reactions of carbon monoxide and nitrogen oxides have great technical importance in the field of exhaust gas purification for the control of their emissions. Zeolite encapsulated ruthenium complexes catalyse the reaction between nitric oxide and ammonia to form nitrogen while water gas shift and Fischer-Tropsch reactions are reported for carbon monoxide. Cobalt phthalocyanine in NaY was found to be more efficient for the oxidation of carbon monoxide by oxygen than free cobalt phthalocyanine complex.
In literature, both homogeneous\textsuperscript{251} and heterogeneous\textsuperscript{252} catalyst systems were reported for oxyhalogenation of aromatics. The former poses environmental problems in disposing used catalysts whereas the latter is inconvenient as it is a two stage process operating at elevated temperatures. More recently, oxyhalogenation of aromatics over chloro- or nitro-substituted phthalocyanines of Cu, Fe and Co encapsulated in zeolites X, Y and L under near ambient conditions has been reported\textsuperscript{253}. A tremendous increase in the turnover frequency for substrate conversion has been claimed when the complexes are encapsulated in the zeolite cavities.

Most of the catalytic reactions over zeolite encapsulated complexes are redox reactions. A few other types of reactions are also known to occur on zeolite complexes. Shape selective catalysis of certain nickel complexes in the oligomerisation of ethane was described by Keim\textsuperscript{254}. The length of the oligomers could be restricted to $C_{20}$ over zeolite supported complexes, whereas higher carbon numbers are observed over homogeneous systems in solution or supported on amorphous solids. Zeolite encapsulated complexes have also been used in acid-base catalysis\textsuperscript{255}.

1. 10 \textbf{FUTURE OUTLOOK}

The industrial preference of homogeneous catalysts is due to their high activity at low temperatures. Such processes have received much attention also in the wake of high demand for fine chemicals, desire to use new feedstocks and high selectivity for environmental protection. But, nowadays, there is little incentive to develop homogeneously catalysed industrial processes, mainly because of economic factors and operational difficulties. However, the excellent catalytic properties of homogeneous catalysts promise an optimistic prognosis.

The immobilization of homogeneous catalysts has been one of the major areas of investigation in scientific and industrial research for developing improved technologies which are cost effective and convenient for operation. Zeolite encapsulated metal complexes have been the main focus in the search for effective heterogenized systems.
Furthermore, their structural similarities with natural metalloenzymes have simulated a special interest. These systems are named as 'Zeozymes'.

Further development in this biomimetic catalysis by zeolite complexes could possibly focus on the following:

1. Variation of central metal atom of the encapsulated complex
2. Encapsulation of complexes with new ligands
3. Use of molecular sieves of extra large pores
4. Application in new chemical reactions
5. Scale up for commercial use in chemical industries

It is known that certain transition metals are particularly suitable for specific reactions. Furthermore, the electronic and stereochemical properties and hence the catalytic activity of metal complexes are dependent on the nature of the metal. Hence the role of metal ions in the encapsulated complex has to be investigated for optimising the catalytic activity. The nature of ligand also influences the electronic and steric structure of the encapsulated complex. Therefore, the modification of the ligand structure may lead to the development of a stereoselective intrazeolite complex catalyst. The interaction of zeolite matrix on encapsulated complexes has also to be considered while designing such catalysts.

Zeolite support plays an effective role in inducing selectivity in catalytic reactions over intrazeolite complexes. Zeolites like NaY, NaX, ZSM-5 and ALPO-5 have been used by previous workers for supporting metal complexes. The microporous cavities (6-13 Å) of these zeolite hosts limit the size of guest molecules to be encapsulated. Mesoporous sieves such as MCM-41 and FSM-16 consisting of honeycomb structures with numerous channels of 20-100 Å diameter are attractive for encapsulating bulky molecules. Such zeolite complexes are accessible to larger substrates and hence can catalyse reactions involving them.
Zeolite encapsulated complexes exhibit catalytic activity comparable to their homogeneous counterparts. These systems would be suitable for highly selective chemical transformations which are difficult on other types of catalysts. The reactivity of zeolite complexes obtained by the combination of the activity of encapsulated complex and the selectivity due to the complex and the zeolite framework, and operational benefits of these heterogenized systems can be exploited in the vast area of fine chemical and organic synthesis.

In addition to the requirements which are fundamental for catalytic performance, an industrial catalyst must have properties which ensure successful implementation in chemical processes. The shape, dimension and mechanical stability are some of such properties to be optimised by trial-and-error experiments. The scale up of zeolite encapsulated complexes for commercial utility would be a new milestone in the history of catalysis.

1.11 SCOPE OF THE PRESENT STUDY

The challenge of developing new technologies for fulfilling the demands of modern society can be addressed by the science and technology of catalysis as it plays a key role in modern industrial processes. Success depends on the development of novel, active, selective and stable catalysts which can perform uniquely at milder conditions. The environmental and economic pressures have also emphasized the need for efficient catalysts with improved characteristics. The thrust on the development of powerful catalysts and the desire to comprehend the science behind their catalysis are reflected in the recent spurt of research publications. Two areas which have received wide attention for innovative research are: (i) heterogenization of homogeneous transition metal complex catalysts and (ii) modification of conventional metal oxide catalysts to tailor them to effectively catalyse specific reactions. The present investigation has been confined to these two areas.
Among the heterogenized metal complex catalysts, studies on zeolite encapsulated complexes appear to be more challenging and interesting as they provide ways to explore the shape selectivity of zeolite support and inhibit the deactivation processes of metal complexes. These systems are also attractive in a biomimetic perspective due to their structural resemblance to natural metalloenzymes. Therefore, our studies are limited to the synthesis, characterization and evaluation of catalytic activity of some zeolite encapsulated complexes. Characterization of zeolite encapsulated complexes are often very difficult. In most cases, characterization has been based on the structures of the simple complexes. We have thus chosen, ligand systems, whose simple complexes have already been studied. The following are the ligands selected for the present study:

1. Dimethylglyoxime
2. 3-formylsalicylic acid
3. N,N'-ethylenebis(7-methysalicylideneamine)
4. N,N'-ethylenebis(5,6-benzosalicylideneamine)

A search through literature has clearly revealed that zeolite encapsulated complexes of these ligands have not yet been studied. The following have been the objectives of the present investigation:

1 To synthesize and characterize zeolite encapsulated transition metal complexes.
2 To examine the effect of zeolite framework on the structure and geometry of the complexes.
3 To study the thermal stability of zeolite complexes.
4 To evaluate the catalytic activity of zeolite complexes for the decomposition of hydrogen peroxide and for the oxidation of benzyl alcohol, ethylbenzene and 4-methoxybenzaldehyde.
We have also attempted the modification of a supported metal oxide catalyst. Metal oxide catalysts have found numerous industrial applications in a variety of chemical processes. The studies on the nature of active sites and fine tuning them for better performance of the catalyst are the main tasks in the catalyst development. Modification of active sites can be achieved by incorporating small amounts of suitable additives which can impart the desired characteristics for a particular reaction. Cu-Cr/Al₂O₃ is widely studied as a metal oxide catalyst for CO oxidation. This catalyst is attractive as a model system to illustrate the above mentioned approach for improving metal oxide catalysts. The additives, CeO₂ and TiO₂ have been used in the present study for modifying Cu-Cr/Al₂O₃ catalyst. The investigations on the metal oxide catalyst have focused on the following:

1. To ascertain the role of Cu and Cr in the carbon monoxide oxidation and the effect of Cr on the stability of the catalyst to withstand severe thermal and hydrothermal conditions
2. To examine the effect of additives, TiO₂ and CeO₂, on oxidation activity and stability.
3. To identify different crystal phases and evaluate their influence on catalytic performance
4. To investigate the influence of active metal dispersion on oxidation efficiency

There is a growing interest to design and produce metal oxide catalysts for replacing highly expensive noble metal catalysts for applications such as gas purification via CO oxidation. Modified Cu-Cr catalysts are expected to provide a welcome replacement of noble metal catalysts.
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