

**STUDIES ON SOME SUPPORTED TRANSITION  
METAL COMPLEX AND METAL OXIDE CATALYSTS  
FOR OXIDATION REACTIONS**

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**By**

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## **dedicated to my loving parents**


" When you know a thing, to hold that you know it, and when you don't know a thing, to allow that you don't know it, this is the true knowledge. "

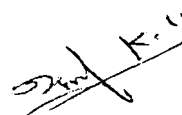
Confucius, 551-479 BC

12<sup>th</sup> June, 2000

## CERTIFICATE

This is to certify that this thesis is an authentic record of research work carried out by Mr. K. O. Xavier under our supervision, in partial fulfillment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

  
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## DECLARATION

I hereby declare that the work presented in this thesis entitled " Studies on some supported transition metal complex and metal oxide catalysts for oxidation reactions " is entirely original and was carried out by me independently under the supervision of Prof. Jacob Chacko, Department of Chemical Oceanography and Prof.K.K. Mohammed Yusuff, Department of Applied Chemistry, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for the award of any degree.



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12<sup>th</sup> June, 2000

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## PREFACE

The application of catalytic science envisages the production of materials and development of processes which address the critical needs of society through economic growth and environmentally sustainable progress. Though homogeneous catalysts have the potential to achieve these targets through efficient, selective chemical transformations at milder conditions, it has grown only at a slower rate due to economic and technical limitations. Heterogenization of homogeneous catalysts has emerged as a welcome alternative. However, efforts are still required to refine the conventional heterogeneous systems like metal oxide catalysts to maximize the yield of desired product at commercially more acceptable conditions.

Zeolite encapsulated transition metal complexes have received wide attention as an effective heterogenized system that combines the tremendous activity of the metal complexes and the attractive features of the zeolite structure. Zeolite encapsulated complexes offer a bright future for attempts to replace homogeneous systems retaining its catalytic activity and minimizing the technical problems, especially for the partial oxidation of organic compounds. Studies on some zeolite encapsulated transition metal complexes are presented in this thesis. The ligands selected are technically important in a bio-mimetic or structural perspective. Attempts have been made in this study to investigate the composition, structure and stability of encapsulated complexes using available techniques. The catalytic activity of encapsulated complexes was evaluated for the oxidation of some organic compounds. The recycling ability of the catalyst as a result of the encapsulation was also studied.

Our studies on Cu-Cr/Al<sub>2</sub>O<sub>3</sub>, a typical metal oxide catalyst, illustrate the use of design techniques to modify the properties of such conventional catalysts. The catalytic activity of this catalyst for the oxidation of carbon monoxide was measured. The effect of additives like CeO<sub>2</sub> or TiO<sub>2</sub> on the activity and stability of this system was also investigated. The additive is potent to improve the activity and stability of the catalyst so as to be more effective in commercial usage.

The thesis is structured into eight chapters. Chapter I gives a comprehensive account of the attractive features of zeolite encapsulated complexes. The experimental techniques used in the present study are described in Chapter II. The chapters III to VI deal with the synthesis and characterization of zeolite encapsulated complexes. The catalytic activity studies of the zeolite encapsulated complexes are discussed in Chapter VII. Chapter VIII gives the details regarding the catalytic studies on the metal oxide catalyst. A gist of the conclusions arrived at on the basis of our investigation is provided at the end of the thesis.



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**CHAPTER I**

**GENERAL INTRODUCTION**

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## **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<sup>1, 2</sup>, application of molecular sieves for better selectivity<sup>3</sup> and alternative chemical routes via catalytic oxidation, hydroxylation, etc. for fine chemical<sup>4, 5</sup> 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<sup>6, 7</sup> and heterogeneous<sup>8-10</sup> 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<sup>11</sup> 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<sup>12</sup>.

Another interesting achievement in this field was the use of Reppe reactions for the commercial production of various chemicals<sup>6</sup>. 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.



$\text{HNi(CO)}_3\text{X}$ , 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 ( $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3$ ,  $\text{H}_3\text{PO}_4$ ) 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<sup>6</sup>. A similar acid catalysed reaction is Koch synthesis<sup>6</sup> 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  $\text{C}_6\text{-C}_{10}$  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<sup>13</sup>. 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,  $\text{RhCl(PPh}_3)_3$ , widely known as Wilkinson's catalyst, can be used for the hydrogenation of olefins<sup>14</sup>. Also, the complexes such as  $\text{RhH(CO)PPh}_3$  catalyse hydroformylation of propene to n-butraldehyde at 10-20 atm and give a yield of > 90% for the linear product, whereas  $\text{Co}_2(\text{CO})_8$  catalyst performs this reaction only at high pressures ( ~200 atm ) and produces a lower yield of 70%<sup>15</sup>. 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<sup>16</sup>. A similar example is the use of rhodium complexes for oxo-process in presence of triphenylphosphine as co-catalyst<sup>6</sup>. 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<sup>6, 7</sup>, the shell process with nickel-phosphine catalysts<sup>6, 17</sup> and the Ethyl process with the classical Ziegler trialkylaluminium catalyst<sup>7, 13</sup> are some of the industrially important homogeneous processes for ethylene oligomerisation. Homogeneous oxidation catalysis<sup>6</sup> 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<sup>18</sup>.

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<sup>6</sup>. In addition, Monsanto has introduced a process<sup>15</sup> 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<sup>19</sup>. Some of the recent studies have focused on the use of homogeneous catalysts for regioselective and enantioselective reactions<sup>20, 21</sup>. 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<sup>22-24</sup>, 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<sup>25, 26</sup>. 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<sup>27, 28</sup>. 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<sup>29</sup>. CuO-ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is also used for water gas shift reaction in fertilizer plants<sup>30</sup>. 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<sup>31</sup>.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported oxides of Mo or W, promoted with oxides of Co or Ni are used for the hydrotreating of petroleum fractions<sup>32</sup>. 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<sup>33</sup>. Some of the other catalytic processes in this class are ammoxidation of propylene to acrylonitrile over silica supported bismuth-molybdate catalyst<sup>34</sup>, oxidation of methanol to

formaldehyde over iron molybdate <sup>35</sup>, hydrolysis of acrylonitrile to acrylamide and hydrogenation of nitrobenzene to aniline over Cu based catalysts <sup>10</sup>, oxidative coupling of methane by Li doped MgO <sup>36</sup>, Fischer-Tropsch synthesis over CuO-ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts <sup>37</sup>, Claus process by alumina catalysts <sup>10</sup>, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysed oxidation of o-xylene to phthalic anhydride <sup>10</sup> and selective catalytic reduction of NO<sub>x</sub> over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>/SiO<sub>2</sub> catalyst <sup>38</sup>.

### 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 CeO<sub>2</sub> and alumina stabilized with La<sub>2</sub>O<sub>3</sub> <sup>39, 40</sup>. The support and active components are dispersed on a monolith structure for the effective control of emissions from automobiles <sup>1, 2</sup>. Catalysts containing Pt or Pd were used for the high temperature combustion of flue gases <sup>41, 42</sup>. 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 <sup>43</sup>. 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 <sup>44</sup>. Selective hydrogenation of acetylenes to

corresponding olefins in C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> petrochemical streams is generally carried out on different types of supported Pd catalysts<sup>45</sup>.

Supported Pt catalyst is used for the dehydrogenation of paraffins to olefins<sup>10</sup>. The use alumina supported Ru catalyst for the effective conversion of glucose to sorbitol was reported<sup>46</sup>. A Pt-Rh alloy catalyst is used for the oxidation of ammonia to NO/NO<sub>2</sub> in the manufacture of nitric acid<sup>47, 48</sup>. Another important applications of noble metal catalysts are industrial gas purifications such as deoxo process<sup>49, 50</sup>, oxidation of CO to CO<sub>2</sub><sup>51, 52</sup>, 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 Pt<sup>53</sup>.

#### **1.3.4 Zeolites & Zeolite based catalysts**

Catalysis by zeolites has been extensively studied for a broad range of reactions in the past few decades<sup>3, 54-57</sup>. 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 1959<sup>58</sup>.

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, NO<sub>x</sub> abatement and fine chemical industry<sup>58</sup>. Generally, zeolites show four types of selectivities. They are: (1) reactant selectivity

when pore size limits the entrance of reacting molecules<sup>59</sup>, (2) product selectivity when some of the product formed within the pores are too bulky to diffuse out<sup>59</sup>, (3) restricted transition state selectivity when certain reactions are prevented due to the non-availability of required space for corresponding transition state<sup>60</sup> 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<sup>61</sup>.

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<sup>62-64</sup>. Furthermore, the catalysts produced by modifying nonacidic molecular sieves with acidic guest materials were found industrial applications for shape selective base catalysis<sup>65</sup>. 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<sup>66</sup>.

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<sup>67</sup>. Another interesting system is vanadium exchanged zeolites which was found to be effective for high temperature oxidation, oxyfunctionalisation, oxidation of NO with oxygen<sup>68</sup>, etc. In addition, the recent importance of enantioselective synthesis has led to the development of zeolites that can perform shape selective, asymmetric, heterogeneous catalysis<sup>69</sup>.

#### **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<sup>70</sup>. 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<sup>71-74</sup>. 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<sup>75</sup>. Even though, these complexes have shown catalytic activity, the presence of variety of surface species restrict them to be well defined<sup>76</sup>.

#### **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

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**(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 chloromethylating phenyl rings of the polymer by chloromethyl ethers, then functionalising by reacting with  $\text{LiPPh}_2$  and exchanging with homogeneous catalyst<sup>14</sup>. In the second approach, a metal complex containing desired amount of functionalised ligand reacts with the solid surface to form the supported complex.  $\text{Ni}(\text{CO})_4$ , as an example, was anchored by reacting it with phosphinated silica at optimum experimental conditions<sup>70</sup>. 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<sup>77</sup>.

**(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<sup>78-82</sup>. 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<sup>83-86</sup>. The isomerisation of pentene-1 catalysed by  $\text{RhCl}_3$  supported in a thin film of ethylene glycol and hydroformylation of propene catalysed by  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$  in benzylbutylphthalate film are some the examples of supported liquid phase catalysts<sup>87-88</sup>. Supported aqueous phase catalysts were developed by supporting water/organic solvent biphasic catalysts<sup>89</sup>. 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.

### (3). *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<sup>90-92</sup>. The increase of interlayer spacing provides evidence for intercalation. The enhanced selectivity of intercalated catalysts in reactions indicates the presence of steric effects<sup>92</sup>. The special feature of this system is the possibility to adjust the size of interlayers by incorporating complexes of different sizes<sup>93</sup>, 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.



supported in Y zeolite modified with Li was reported to be particularly active for hydrogenation reactions<sup>99</sup>. The intrazeolite chemistry of iron carbonyls also received much attention.  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$  were adsorbed in Y-zeolite without any change in the structure<sup>100</sup>. Zeolite X or Y supported dicobalt octacarbonyls were prepared by either direct sublimation<sup>101</sup> or adsorption from pentane solution<sup>102</sup>. Nickel tetracarbonyl in zeolite support was also studied<sup>103</sup>.

Zeolites, X and Y allow the entrapment of certain organometallics like bis(dithiophosphato)nickel which cannot be supported on carrier like silica gel<sup>104</sup>.  $\text{Tris}(\pi\text{-allyl})\text{rhodium}$  was a well studied system to illustrate the synthesis of organometallic compounds in zeolite cavities<sup>105</sup>. Metallocenes 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<sup>106</sup>. 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<sup>107</sup>.

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<sup>108-110</sup>. Intrazeolite hexamethylisocyanide complex of Co was one of such well characterized complex<sup>111</sup>. Later, several workers focused on the encapsulation of complexes of monodentate ligands. These studies were first reviewed by Lungford<sup>111, 112</sup> and later on by Mortier and Schoonheydt<sup>113</sup> and Ozin and Gil<sup>114</sup>. 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<sup>115-118</sup>.

### 1.5.2 Structural considerations

Zeolites are microporous, crystalline, three dimensional aluminosilicates composed of  $\text{SiO}_4$  and  $\text{AlO}_4^-$  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  $\text{SiO}_4$  and  $\text{AlO}_4^-$  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<sup>56</sup> are given in Table I. 1.

Table I. 1

Properties of zeolites A, X and Y

Zeolite	Unit cell formula	Mol. ratio $\text{SiO}_2/$ $\text{Al}_2\text{O}_3$	$\alpha$ -cage diameter	$\alpha$ -cage aperture
A	$\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} n\text{H}_2\text{O}$	2 : 1	11 Å	4 Å
X	$\text{Na}_{86}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106} n\text{H}_2\text{O}$	2.5 : 1	13 Å	8 Å
Y	$\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136} n\text{H}_2\text{O}$	5 : 1	13 Å	8 Å

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  $\text{Na}^+$  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.

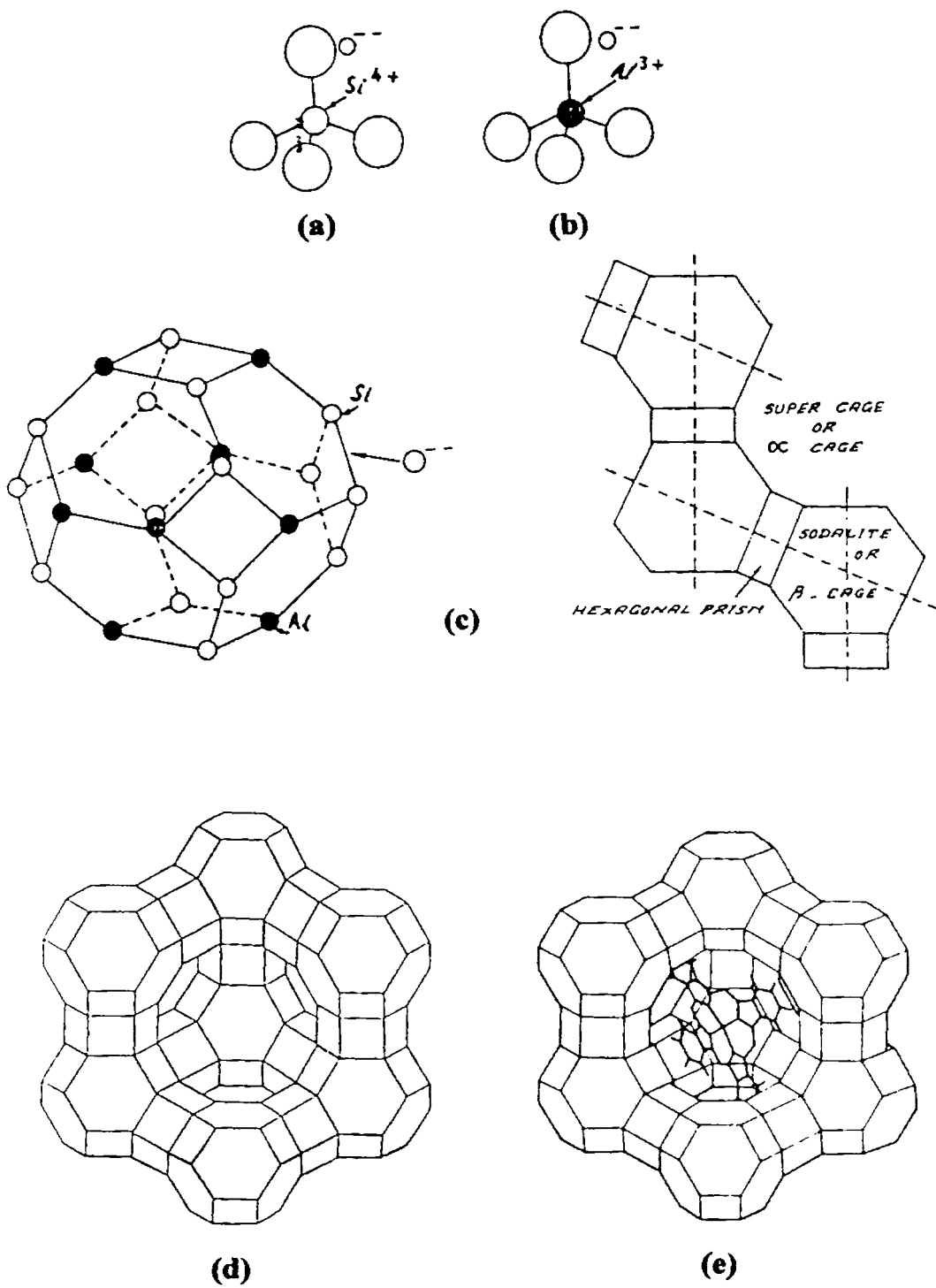


Figure I. 1

(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  $\alpha$ -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<sup>114, 119</sup>. 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.<sup>120</sup>. 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<sup>121</sup>. 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<sup>114</sup>. 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<sup>122-124</sup>. 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<sup>125</sup>. 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<sup>126-128</sup> and later on superstructured mimics<sup>129</sup> 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<sup>130-132</sup>.

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<sup>117, 125, 133</sup>.

Several zeolite complexes were designed and successfully developed to act as zeozymes with respect to activity and stability in catalytic reactions. Nature performs







































































































































































































































































































































































































































