CATALYTIC ACTIVITIES OF METAL COMPLEXES IMMOBILIZED IN ZEOLITE-Y

A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY
in
CHEMICAL ENGINEERING

by

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APRIL, 2007

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **CATALYTIC ACTIVITIES OF METAL COMPLEXES IMMOBILIZED IN ZEOLITE–Y** in partial fulfilment of the requirements for the award of the degree of *Doctor of Philosophy* and submitted in the Department of Chemical Engineering of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from July, 2004 to April, 2007 under the supervision of Dr. Shri Chand, Professor, Department of Chemical Engineering and Dr. Mannar R. Maurya, Associate Professor, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

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ABSTRACT

The term “catalyst” was first introduced by Brezelius in 1835, Catalysts help the reaction to achieve the chemical equilibrium by reducing the potential energy barrier in the reaction path. Catalyst activates the reactant molecules to bind with it at milder conditions where they react and finally products separate out leaving the catalyst for the next cycle. As large as 95 % processes used in the chemical industries today are catalyst based technologies. Directly or indirectly catalysts have contributed to more than 20 % GDP of developed nations. Important properties of the industrial catalysts are the substantial working life and the retention of their effectiveness while environmental issues stress on the development of such catalytic processes that are beneficial from industrial as well as environmental point of view. The efficient use of the solid supported catalysts can go a long way towards achieving these goals. Various methodologies have been evolved for the immobilization of homogeneous transition metal complexes on the solid support. Encapsulation of homogeneous catalysts in the super cages of zeolite matrix is one of the important methods for the immobilization. This method has provided opportunity to develop catalytic processes in the synthesis of fine chemicals and being used in various types of catalytic reactions like alkylation, hydrogenation, dehydrogenation, hydro-cracking, cyclization, amination, acylation, isometization, rearrangement and oxidation. The catalytic oxidations of organic substrates have been studied well due to its commercial and synthetic importance of the resulted functionalized molecules. An encouragement is thus derived to synthesize various zeolite encapsulated metal complexes and use them as catalysts for the oxidation of different organic substrates.

The present thesis describes the synthesis of metal complexes with potential coordinating organic ligands encapsulated in the nano-cavity of zeolite-Y and their characterization by various physico-chemical techniques. Different types of catalytic oxidation reactions have been carried out and suitable reaction conditions have been obtained for the maximum oxidation of organic substrates. The reaction products have been analyzed by gas chromatograph (GC) and their identities confirmed by GC-MS.

For convenience the work presented in the thesis has been divided in the following chapters.

First chapter is the introductory one and describes various types of solid inert support that have been used for the immobilization of homogeneous catalysts. A brief introduction of zeolites and their importance, different methods for the immobilization of metal complexes in the nano-cavities of zeolites have been described. Literature on the catalytic applications of various encapsulated metal complexes has also been reviewed.

Second chapter describes the interaction of oxovanadium(IV) exchanged zeolite-Y with the Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole (Hsal-ambmz) in refluxing methanol followed by aerial oxidation leads to the formation of encapsulated dioxovanadium(V) complex, [VO_2(sal-ambmz)]-Y(**2.1**). Similar reaction with copper(II) exchanged zeolite-Y gave encapsulated copper(II) complex, [Cu(sal-ambmz)Cl]-Y(**2.2**). These encapsulated complexes have been characterized by spectroscopic studies, thermal analysis and scanning electron micrographs (SEM) as well as X-ray diffraction patterns. 3D model structure generated for neat complex [VO_2(sal-ambmz)] suggests that zeolite-Y can accommodate these complexes in its nano cavity without any stain. The encapsulated materials are found to be active catalysts for the oxidation of phenol, styrene and methyl phenyl sulfide using H_2O_2 as an oxidant. Under the optimised reaction conditions about 42 % conversion of phenol was obtained with these catalysts where the selectivity of catechol varied in the order: **2.2** (73.9 %) > **2.1** (65.2 %). With the conversion of 97.0 % with **2.1** or 56.7 % with **2.2**, the oxidation of styrene gave styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde as major products. A maximum of 96.1 % (with **2.1**) and 91.0 % (with **2.2**) conversion of methyl phenyl sulfide was observed in which the selectivity of major product methyl phenyl sulfoxide was found to be ca. 98 %.

Reaction of N,N′-bis(salicylidene)cyclohexane-1,2-diamine (H_2sal-dach) with oxovanadium(IV) and copper(II) exchanged zeolite-Y in refluxing methanol to yield the corresponding zeolite-Y encapsulated metal complexes, abbreviated herein as

[VO(sal-dach)]-Y (**3.1**) and [Cu(sal-dach)]-Y (**3.2**) have been described in **Chapter three**. Spectroscopic studies (IR, electronic and ^1H NMR), thermal analysis, scanning electron micrographs (SEM) and X-ray diffraction patterns have been used to characterise these complexes. 3D model structure generated for neat complex [VO(sal-dach)] (**3.3**) suggests that zeolite-Y can accommodate these complexes in its nano cavity without any stain. These encapsulated complexes catalyse the oxidation of styrene, cyclohexene and cyclohexane efficiently in good yield using H_2O_2. Under the optimized conditions, the oxidation of styrene catalysed by [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y gave 94.6% and 21.7% conversion, respectively, where styreneoxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde being the major products. Oxidation of cyclohexene catalysed by these complexes gave cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as major products. Conversion of cyclohexene achieved was 86.6% with [VO(sal-dach)]-Y and 18.1 % with [Cu(sal-dach)]-Y. A maximum of 78.1 % conversion of cyclohexane catalysed by [Cu(sal-dach)]-Y and only 21.0 % conversion by [VO(sal-dach)]-Y with major reaction products of cyclohexanone, cyclohexanol and cyclohexane-1,2-diol have been obtained.

Chapter four deals with the encapsulation of oxovanadium(IV), copper(II) and nickel(II) complexes of Schiff base derived from salicylaldehyde and o-aminobenzyl alcohol (H_2sal-oaba) in the nano pores of zeolite-Y by flexible ligand method and characterized by metal analysis, spectroscopic (IR and electronic) studies, scanning electron micrographs, thermal analysis and X-ray diffraction patterns. The encapsulated complexes abbreviated here as [VO(sal-oaba)(H_2O)]-Y (**4.1**), [Cu(sal-oaba)(H_2O)]-Y (**4.2**) and [Ni(sal-oaba)(H_2O)$_3$]-Y (**4.3**) catalyze the oxidation of styrene, cyclohexane and methyl phenyl sulfide using H_2O_2 as oxidant in good yield. Styrene catalysed by [VO(sal-oaba)(H_2O)]-Y, [Cu(sal-oaba)(H_2O)]-Y under optimized reactions gave five reaction products, namely, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde, while [Ni(sal-oaba)(H_2O)$_3$]-Y gave benzaldehyde selectively. In the presence of *tert*-butylhydroperoxide all catalysts gave styrene oxide in major yield, though overall conversion has been found low (10 – 30 %). The oxidation products of cyclohexane are cyclohexanone and cyclohexanol. A maximum of 93.2 % conversion of methyl phenyl sulfide has been achieved with [VO(sal-oaba)(H_2O)]-Y using H_2O_2 as oxidant, where selectivity of sulfoxide was 96.9 %. Other catalysts were inactive towards the oxidation of methyl phenyl sulfide. Neat complex [VO(sal-oaba)(H_2O)] has been equally active.

Encapsulation of oxovanadium(IV) and copper(II) complexes of monobasic bidentate NS donor ligand, 2-mercaptomethylbenzimidazole (Htbmz) in the cavity of zeolite-Y by flexible ligand method have been described in **Chapter five**. These complexes have been characterized by various physico-chemical methods. These encapsulated complexes, abbreviated as [VO($tbmz)_2$]-Y (**5.1**) and [Cu($tbmz)_2$]-Y (**5.2**), have been used as catalysts for the oxidation of styrene, methyl phenyl sulfide and diphenyl sulfide. Under the optimized reaction conditions, [VO($tbmz)_2$]-Y gave 96.4 % conversion of styrene with four oxidation products, styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde. Conversion with [Cu($tbmz)_2$]-Y is considerably low (36.9 %) and gave only four products, styrene oxide, benzaldehyde, benzoic acid and phenylacetaldehyde. In both cases formation of benzaldehyde is relatively high. These catalysts are very active for the oxidation of methyl phenyl sulfide and diphenyl sulfide. The oxidation of diphenyl sulfide required at least H_2O_2 to diphenyl sulfide ratio of 3:1 to give 91.7 % conversion in 7 h of reaction time. However, 94.3 % conversion of methyl phenyl sulfide has been achieved within 3 h of contact time at substrate to H_2O_2 ratio of 1:1. The catalytic activity of neat complexes using similar molar concentration as that used for encapsulated complexes under above reaction conditions have also been tested for comparison. It has been observed that the corresponding neat complexes have shown equally good catalytic activities. But high turn over frequency and recyclability make the zeolite encapsulated complexes better then their neat analogues.

Acknowledgments

I would like to take this opportunity to pay my regard and a deep sense of gratitude to Dr Shri Chand, Professor & Head, Department of Chemical Engineering, and Dr. M. R. Maurya, Associate Professor, Department of Chemistry, whom help, brilliant creativity and enthusiasm have guided this research work from its conception to its completion. I thank them for their continued responsiveness to my needs, and for being so professional and friendly through the process. I also acknowledge them for taught me the value of time in my life. I wish to express my sincere thanks.

I am thankful to Professor B. Mohanti, Former Head of the Department of Chemical Engineering for encouragements. I would like to express my profound gratitude to Professor I. M. Mishra and Dr. B. Prasad for encouragement during research work. I am thankful to Professor Ravi Bhusan, Head of the Department of Chemistry for providing me necessary facilities.

I would like to express my acknowledgment to Mr. Ayodhya Prasad Singh for his instant help in all kind of work. I also acknowledge Mr. Tara Chand, Mr. Satpal and Mr. Abdul Haque, Mr. Shadab technical and non technical staff for their help.

I also acknowledge Mr. Akhilesh Sharma, Mr. Raj Kumar and Mr. Narendra of our Department Computer Center for providing computer facility.

I express my sincere thank to Head, Institute Instrumentation Center of our institute for providing necessary instrumentation facility. My special thanks to Mr. Anil Saini and Mr. Rajiv Juyal for recording TGA- DTA and AAS of my samples. I also acknowledge Mrs. Rekha Sharma and Mr. Shiv Kumar for SEM and XRD analysis of my samples.

I own my special thanks to my lab mate Dr. Sweta for their selfless support and suggestions during my last stage of work. I extend my warm appreciation to my other lab mates Pradeep, Maneesh, Arti, Aftab, Umesh, Baljit and Manisha for their company and motivation to complete my work.

I extend my warm appreciation to my friends specially M. Anil, Siraj, Arvind, Anil Mathur, Upendra and Praveen for company, moral support and valuable time in hours of need.

I thank my mummy and papa for giving me that much love and appreciation for the accomplishment of my work. I thank my brother Premendra for his love and admiration, which continue to support me through my difficult times. I thank my younger sisters Swati and Smriti for her love and appreciation. Lastly I thank to my nice Sanya for her cute and charming conversations, from which forget about my all tensions and stress.

I have no words for my dear wife Reenu for her deepest love, support, and encouragement, positive spirit and strength have inspired me to be the best I can be.

LIST OF PUBLICATIONS

1. M. R. Maurya, A. K. Chandrakar and S. Chand
   Oxidation of phenol, styrene and methyl phenyl sulfide with H_2O_2 catalysed by dioxovanadium(V) and Copper(II) complexes of 2-aminomethylbenzimidazole based ligand encapsulated in zeolite-Y, *J. Mol. Catal. A: Chem.*, 263, 227 (2007).

2. M. R. Maurya, A. K. Chandrakar and S. Chand
   Oxovanadium (IV) and copper(II) complexes of 1, 2-diaminocyclohexane based ligand encapsulated in zeolite-Y for the catalytic oxidation of styrene, cyclohexene and cyclohexane, *J. Mol. Catal. A: Chem.*, 270, 225 (2007).

3. M. R. Maurya, A. K. Chandrakar and S. Chand
   Oxidation of phenol, styrene and methyl phenyl sulfide with H_2O_2 catalysed by dioxovanadium(V) and Copper(II) complexes of 2-aminomethylbenzimidazole based ligand encapsulated in zeolite-Y, *National symposium on modern trends in chemical sciences*, Kurukshetra University Kurukshetra, OP-10 (2006).

4. M. R. Maurya, A. K. Chandrakar and S. Chand
   Zeolite-Y encapsulated metal complexes of oxovanadium(VI), copper(II) and nickel(II) as catalyst for the oxidation of styrene, cyclohexane and methyl phenyl sulfide, Communicated.

5. M. R. Maurya, A. K. Chandrakar and S. Chand
   Oxidation of methyl phenyl sulfide, diphenyl sulfide and styrene by ovovanadium(IV) and copper(II) complexes of NS donor ligand encapsulated in zeolite-Y, Communicated.

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CHAPTER-1

General introduction

1.1. INTRODUCTORY

Catalysts help the reaction to achieve the chemical equilibrium by reducing the potential energy barrier in the reaction path. Brezelius introduced the term "catalyst" in 1835. Catalysis has been an important area of research since then and continuous efforts have been made to understand and utilize the phenomenon for practical purposes. Catalysts activate the reactant molecules to bind with it at milder conditions where they react and finally products separate out leaving the catalyst for the next cycle; Figure 1.1.

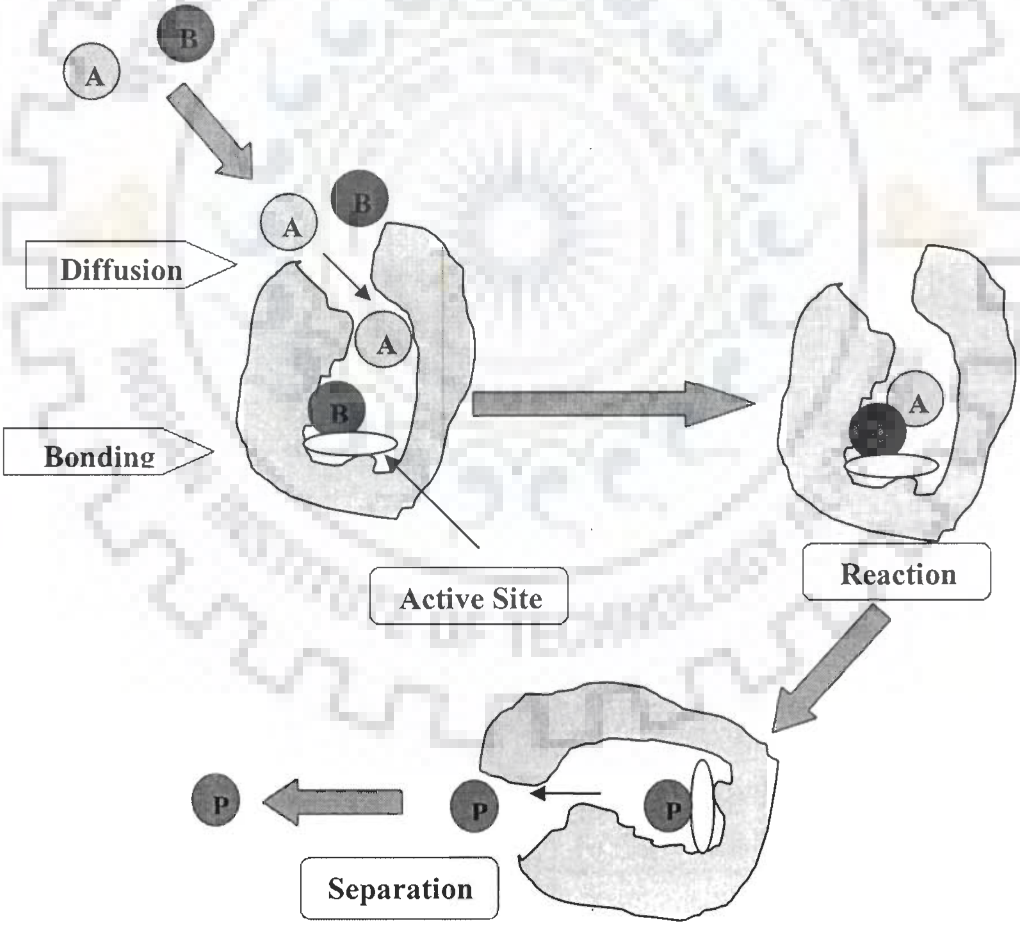


Figure 1.1. Model showing the complete catalytic reaction.

The catalytic reaction occurs at the specific sites called "active site" and rate of the reaction can be significantly improved by enhancing the surface area of the catalyst which in turn enhances the availability of the active sites. Normally, the speed of the catalytic reaction is presented in terms of a "Turn-over Rate" (TOF), which is defined as number of moles of substrate converted on an 'active site' or on a unit catalytic surface area per second at a given condition. In 20th century catalysts have played a vital role as 95 % processes used in the chemical industries today are catalysts based technologies. Directly or indirectly catalysts have contributed more than 20% GDP of developed nations. Major catalyst based technologies for the past 50 years are given in Table 1.1 chronologically.

Table 1.1. Major catalytic technology developments during the past 50 years[a]

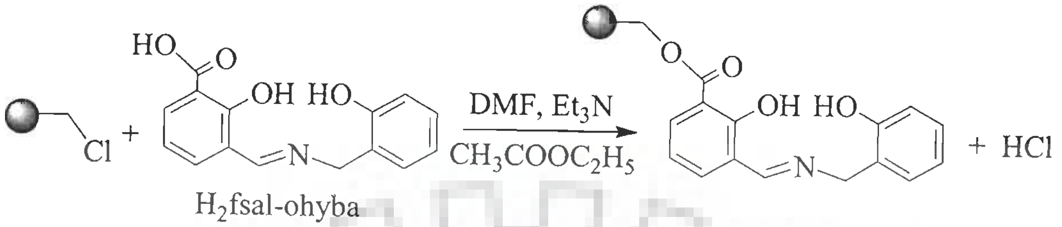
Year	Process	Catalyst
1949	Monometallic reforming	Pt-Al_2O_3
1957	Polymerization	Zeigler-Natta
1962	Steam reforming	Ni-K- Al_2O_3
1964	Zeolite catcracking	X,Y-zeolites
1967	Bimetallic reforming	Pt-Re / Pt-Ir
1968	Selectoreforming	Erionite
1972	Low pressure CH_3OH	Cu-Zn- Al_2O_3
1974	Acetic acid (carbonylation)	Rh-I
1976	Auto emission control	Pt- Al_2O_3
1980	Gasoline from methane	ZSM-5
1982	Auto emission; stack gas	Pt-Rh; V_2O_5-TiO_2
1988	Selective oxidation	Ti-silicates
1988	Chiral catalysts	Cinchonidine-Pt; BINAP
1991	Polymerization	Metallocenes

[a] Adopted from: [1].

Important properties of the industrial catalysts are the substantial working life and the retention of their effectiveness while environmental issues stress on the development of such catalytic processes that are beneficial from industrial as well as environmental point of view. Amongst the variety of catalytically active species known, the transition metal complexes catalyze a wide range of chemical reactions such as oxidation, hydrogenation, polymerization etc. However, these homogeneous catalysts produce a large amount of undesired products that may cause serious problem to the environment. There is, therefore, a need to find more efficient catalytic system, especially for fine chemicals industry and also to meet the environmental challenges. Many efforts have been directed in past two decades towards the development of heterogeneous processes and the heterogenization of known active as well as new homogeneous catalysts [2]. The heterogenization of homogeneous catalysts can be achieved by immobilization, grafting, anchoring or encapsulating them in an inert solid like organic polymer or inorganic support. Their polymerization may also provide heterogenized catalysts.

1.2. SUPPORTS USED FOR CATALYSTS

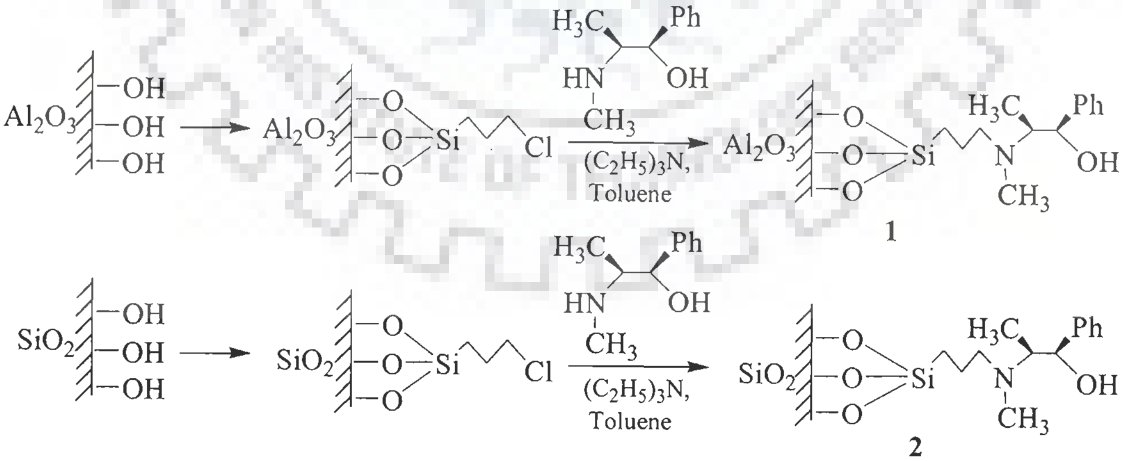
All kinds of materials that are thermally stable and chemically inert can be used as support for catalyst. The functionalized polymers (cross-linked as well as non-cross-linked) have widely been used as support for homogeneous catalysts through covalent bonding. Metal complexes as such may form covalent bond if suitable coordinating site is present on the functional group. Functionalized group of polymer may also react with organic molecules having suitable coordinating site(s) followed by its coordination with metal ions to give polymer-supported metal complexes. The polymer-bound organic molecules having suitable coordinating sites are also called polymer-anchored ligands and their complexes are called polymer-anchored complexes. Complete recoveries of the catalytic reaction products are thus possible. Besides, regeneration and recyclability make them commercially beneficial. One of the most straightforward methods is the reaction of –CH_2Cl group of chloromethylated polystyrene with organic molecules bearing functional groups such as carboxylic, sulfonic and hydroxyl groups [3-6]. Scheme 1.1 represents the synthetic approach [6].



Scheme 1.1

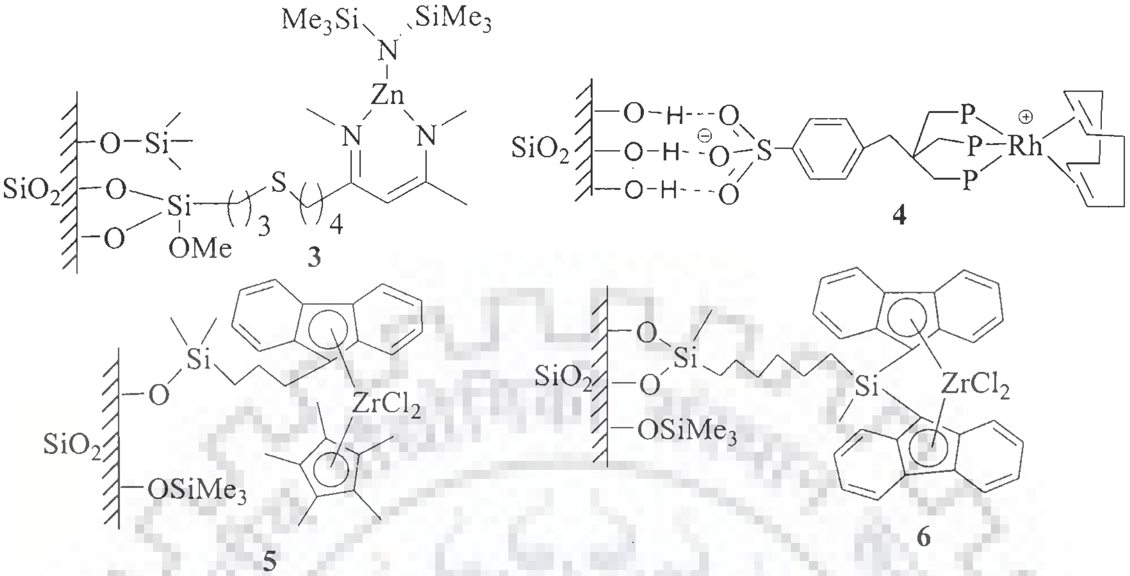
Amongst various inorganic supports, alumina and silica are the most common. One of the oldest methods to prepare supported catalysts is the co-precipitation of the catalytically active component and the support to give a mixture which is subsequently dried, calcined and reduced to give a porous material with a high surface area. Another but most preferred method is loading pre-existing support materials in the form of shaped bodies with the catalytic active phase by means of impregnation or precipitation from solution [7].

Alumina and silica gels have been modified to immobilize various catalysts by direct reaction of surface hydroxyl groups with reactive species; Scheme 1.2 [8].



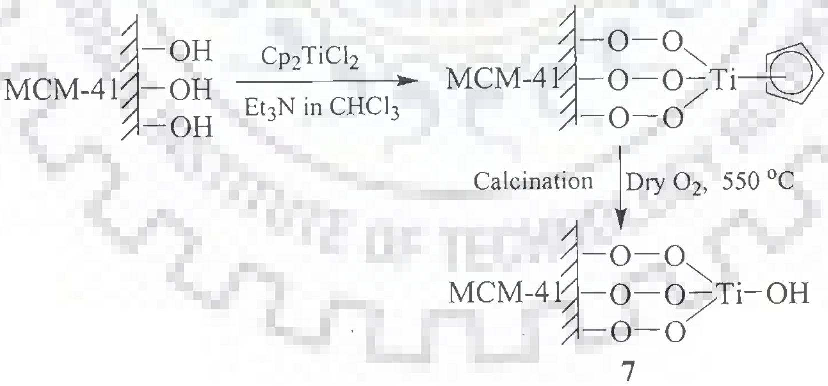
Scheme 1.2. Immobilization of catalysts on silica and alumina.

Other examples of immobilized catalysts are given in Scheme 1.3 [9, 10].



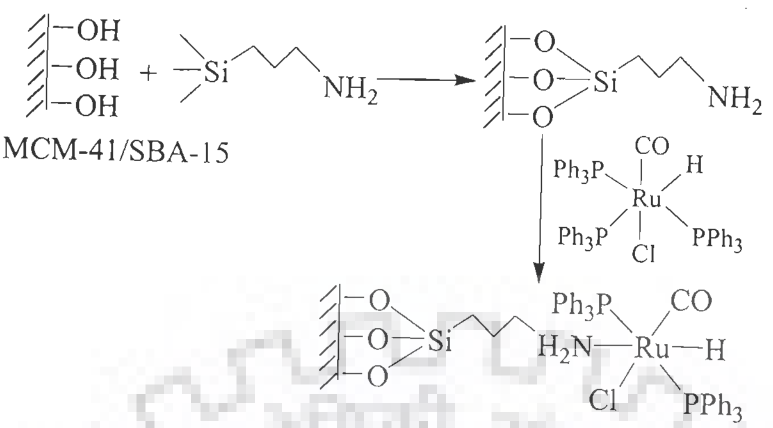
Scheme 1.3

Due to the presence of hydroxyl groups on the surface of mesoporous molecular sieves such as Si-MCM-41 and Si-SBA-15, these materials have also been used for the immobilization of catalysts. Immobilization of titanocene dichloride has been achieved according to the procedure shown in Scheme 1.4 [11].



Scheme 1.4

Halligudi *et al.* have reported the anchoring of [RuH(CO)(PPh$_3$)$_3$Cl] [12] and [VO(saldien)] (H$_2$saldien = N,N′-bis(salicylidene)diethylenetriamine on SBA-15 [13] by functionalizing it as shown in Schemes 1.5 and 1.6.



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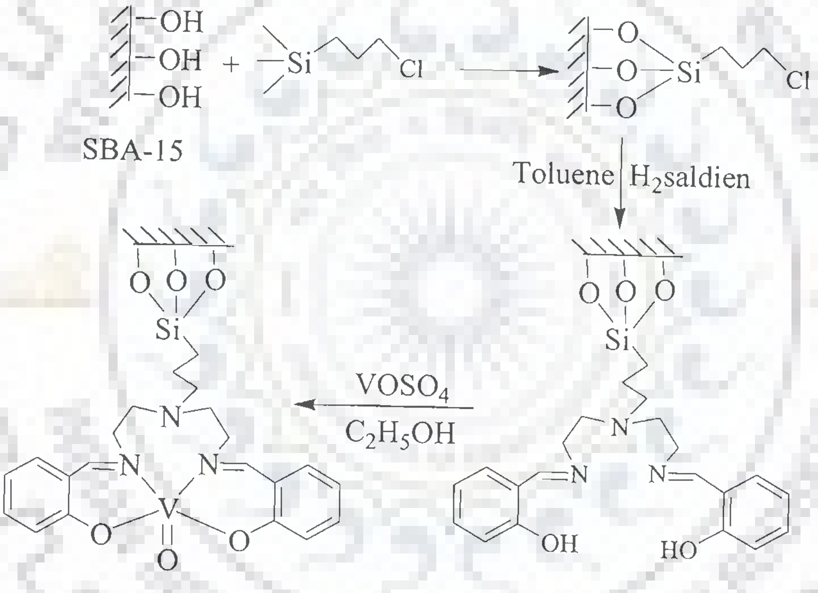
Scheme 1.5



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Scheme 1.6

Recent review article by Jacobs *et al.* [14] provides detail accounts of such immobilized complexes. These immobilized catalysts have been suggested to be better over the polymer-anchored catalysts. This is because polymer-anchored catalysts require their swelling in suitable solvent before their use for catalytic reactions.

Transition metal complexes having good catalytic properties have also been immobilized through encapsulation in the super cages of zeolites in order to prepare heterogeneous catalysts with the desired structure and function [15, 16]. This new class of catalysts is called zeolite encapsulated metal complexes (ZEMC) or ship-in-the-bottle complexes. As the metal complex is not bonded to the host, encapsulated metal complex shares many advantageous features of homogeneous catalysts, whereas the zeolite imparts size and shape selectivity to the catalysts.

Details of the zeolites and their use as solid support have been described in the following section.

1.3. ZEOLITES AND THEIR USE AS SOLID SUPPORT TO HOMOGENEOUS CATALYSTS

Zeolites are crystalline hydrated aluminosilicates with open framework structures constructed from AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens. Each oxygen atom is shared by two silicon or aluminum atoms. Nature has provided many zeolites as minerals and plenty of other zeolites have also been synthesized. These large varieties of zeolites are due to the flexibility of Al-O-Si linkage, which depends on the conditions used during their hydrothermal synthesis. Zeolite crystals are porous on a molecular scale and their framework contains regular arrays of channels and cavities of 4 to 15 Å. which are occupied by exchangeable cations and water molecules. The natural faujasite and synthetic X and Y zeolites contain the super cage of ca.13 Å internal diameter which is connected via 12 rings of 8 Å to four other cages in a tetrahedral arrangement. Thus, zeolite-Y has a three-dimensional pore structure with the pores running perpendicular to each other in three dimensional planes; Figure 1.2. Hydrated zeolite-Y is represented by the formula $Na_{56}Al_{56}Si_{136}O_{384}.250H_2O$ where Na^+ balances the formal negative (-1) charge generated by each $[AlO_4]^-$ units. The number of water molecules gives an idea of the volume of the channels in relation to the total volume while Na^+ can be exchanged with other metal ions as well as H^+ reversibly [19, 20].

Zeolites find applications in many scientific disciplines such as inorganic and organic chemistry, biochemistry, physical chemistry, colloid chemistry, mineralogy, geology, surface chemistry, crystallography, catalysis and all types of chemical engineering process technologies. They are often called molecular sieves because the large number of small but identical pores can be used to separate small molecules from large molecules, which can pass through the pores. Thus, the separation of air components, recovery of different hydrocarbons, removing carbon dioxide and small sulfur compounds from natural gases etc. are possible by using zeolites. Zeolites have also been compared with metalloenzymes and hence they are referred to as "zeozymes".

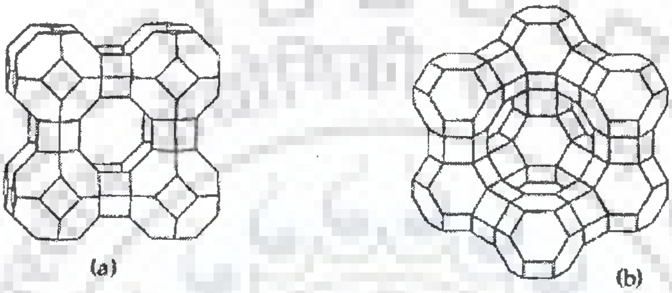
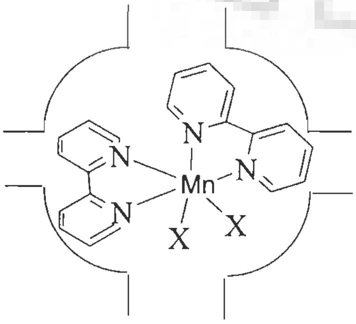


Figure 1.2. Represented zeolite structures: (a) Zeolite A and (b) Zeolite-Y (adopted from Reference [16].

The exchangeable property of extra-framework cations and suitable cavity size of the zeolites allowed their modification by inclusion of chemically interesting molecules. Homogeneous catalyst (i.e. metal complex) may be considered one of such interesting molecules and hence the term zeolite encapsulated metal complexes. A large size of the encapsulated homogeneous catalysts and their rigidity make them difficult to escape out of the zeolite cages; Scheme 1.7. Zeolite encapsulated metal complexes having good catalytic activities possess all the advantages of solid heterogeneous catalysts as well as share many advantageous features of homogeneous catalysts.



Scheme 1.7. Y-super cage with four apertures having encapsulated metal complex

1.3.1. Methods for the synthesis of zeolite encapsulated metal complexes

Bedioui has suggested basically three general approaches to the preparation of zeolite encapsulated metal complexes. These are: flexible ligand method, template synthesis method and zeolite synthesis method. In addition to these, other two approaches, such as, ion exchange method and adsorption method may also be considered. These methods are briefly discussed below [16, 21].

Encapsulation of metal carbonyls by the reaction of metal (e.g. Ru, Rh etc.) exchanged zeolite-Y with CO/H_2 or CO/H_2O to give metal carbonyls is the example of adsorption method. Slow diffusion of small metal carbonyls in to the cavity of zeolite has also been tried. Several metal carbonyls, such as, $Ni(CO)_4$, $Ir_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$ have been encapsulated in zeolite-Y by these methods [22-26].

Peigneur *et al.* encapsulated $[Cu(en)_2]^{2+}$ in faujasites by exchanging small cation e.g. Na^+ present in the cavity of the zeolite with $[Cu(en)_2]^{2+}$ and referred the method as ion exchange method. The complex, $[Cu(en)_2]^{2+}$ can pass through the pore opening of the zeolites [27]. Several such complexes have been prepared in the cavity of zeolites and characterized [28 – 31].

If the ligand is flexible enough to diffuse freely through the zeolite pores, this may react easily with the previously exchanged metal ions in the cavity to give stable metal complexes. The size of the resulting metal complexes will be too large to escape out. Such method is referred to as flexible ligand method. Lunsford *et al.* first applied this method for encapsulation of a series of metal-2,2'dipyridyl complexes [32-34]. Metal-salen complexes are the best examples prepared by this method [16, 35, 36]. Here, the diffusion of ligands has been facilitated mostly in the molten state. Later, suitable solvent has also been used to facilitate the diffusion [37].

In template synthesis method, ligand is synthesized in-situ in the cavity of the zeolite from its constituents in the presence of previously exchanged metal ions. This method has largely been applied to prepare metallophthalocyanines where dicyanobenzene was allowed to diffuse into zeolite cavity through the pores followed by cyclization in presence of previously exchanged metal ions to give complexes [16, 38-44]. In some cases, adsorbed iron pentacarbonyls or ferrocene in Na-Y have been used as starting materials as source of metal ions [39, 43]. Zeolite synthesis method involves the addition of preformed metal complex in a template role to a reaction mixture of starting materials followed by crystallization of zeolite host. This method is advantageous as well defined encapsulated metal complexes under milder conditions can be prepared. This method has been applied to synthesize neutral metallophthalocyanines and metalloprophyrins in the cavity of zeolite-Y [44-46].

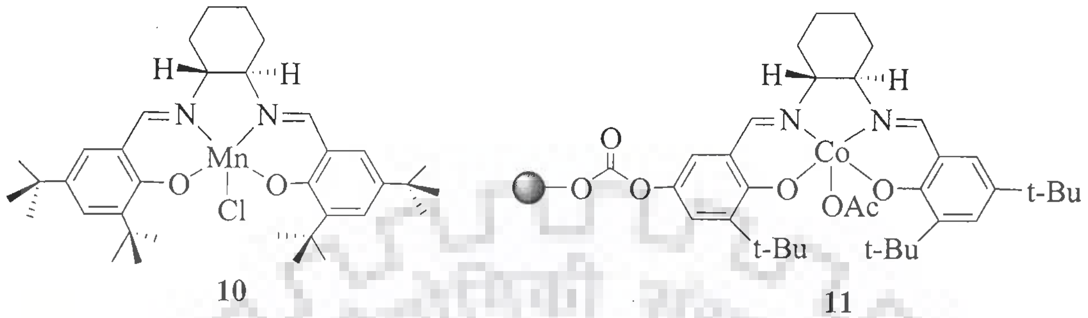
1.3.2. Zeolite encapsulated metal complexes and their catalytic activities

As zeolite encapsulated metal complexes enjoy the advantageous features of homo- as well as heterogeneous catalysts, these materials have provided opportunities to develop catalytic processes for various reactions such as hydrogenation, oxidation, alkylation, cyclization, acylation and isomerisation etc. The methods mentioned in Section 1.3.1 have been very helpful in designing zeolite encapsulated metal complexes and review articles written time to time show the importance of the field. A brief literature survey dealing with selected complexes encapsulated in the cavity of zeolite and their catalytic activity has been presented here.

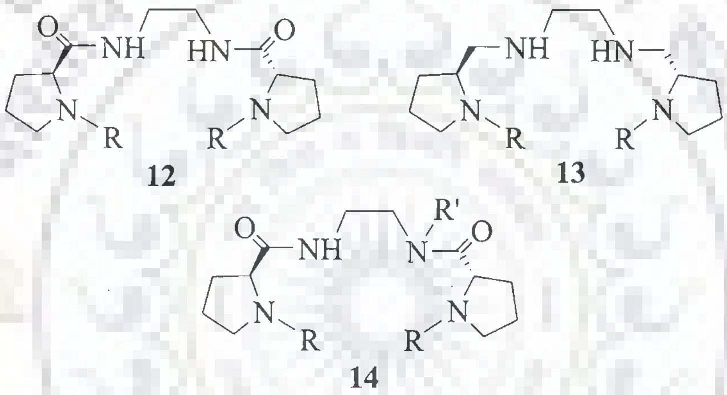
1.3.2.1. Chiral complexes

The catalytic activity of chiral complexes has become a powerful tool in modern synthetic organic chemistry. Jacobson *et al.* have used chiral Mn-salen complexes for the asymmetric epoxidation of a series of unfunctionalized alkenes with high stereo control [47]. Efforts have been made to immobilize Jacobson's type catalysts **(10)** on solid supports. In fact, Jacobsen and Annis have reported derivatized hydroxymethylated polystyrene supported chiral Co(X-sal-dach) complexes **(11)** (H_2-X-sal-dach = Schiff bases derived from *trans*-1,2-diaminocyclohexane and salicylaldehyde derivatives); Scheme 1.8 [48].

Alcón et al. have reported encapsulation of manganese(II) and Cu(II) complexes of chiral ligands **12, 13** and **14** (Scheme 1.9) in zeolite-Y. Encapsulation was affected by flexible ligand method. These encapsulated complexes catalyse the oxidation of methyl phenyl sulfide and (2-ethylbutyl)phenyl sulfide. Conversions of these substrates vary in the range 73 – 100 %. The greater stability of these encapsulated complexes over homogeneous analogues has been attributed to the suppression of dimeric or polymeric species formation [49, 50].



Scheme 1.8



Scheme 1.9

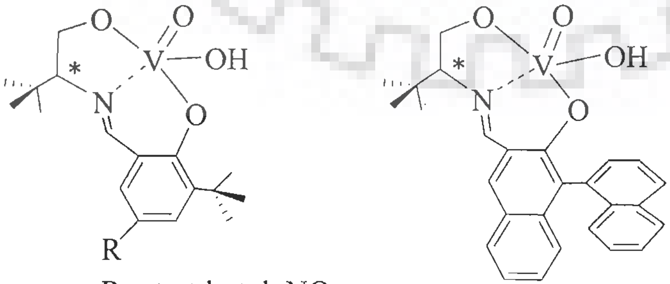
The [Co(salophen)]-Y (H_2salophen = Schiff base derived from 3,5-di-*tert*-butylsalicylaldehyde and *o*-phenylenediamine also been studied as oxygenating agents in the palladium-hydroquinone catalysed aerobic oxidation of 1,3-dienes. It is also active for the aerobic oxidation of 1,3-cyclohexadiene to 1,4-diacetoxy-2-cyclohexene at room temperature. Interestingly these catalysts are reusable [51].

1.3.2.2. Model complexes for enzyme mimic

Zeolite-encapsulated metal complexes have been used to mimic enzymatic systems. Metalloporphyrins, metallophthalocyanines and metal-Schiff base complexes model active sites of enzymes especially monoxygenase enzymes of cytochrome P-450 family. The replacement of the protein skeleton of neutral enzymes by a size and shape selective framework of zeolite may provide the best arrangement for the catalytically active centres. Because of these properties zeolite-encapsulated metal complexes are also called inorganic enzymes.

Bedioui has reviewed such oxidation catalysts and oxygen carriers [16]. The methods reported in section **1.3.1** have been used to incorporate all these complexes (metalloporphyrins, metallophthalocyanines and metal-Schiff base complexes). The [Co(salen)]-Y binds oxygen reversibly and separates oxygen from nitrogen in dry air [15]. The frameworks provide extra stability to the complexes and prevent them from dimerisation. Thus, they represent more efficient reversible oxygen carriers than their homogeneous analogues. Similarly, zeolite encapsulated iron phthalocyanines have been used for biomimetic oxidation of hydrocarbon [52].

Vanadium complexes have been considered as biomimetic models of the active site of haloperoxidases. In presence of oxidant like H_2O_2, they form electrophilic peroxo complexes that selectively transfer an oxygen atom to the organic substrates. Even peroxovanadium(V) complexes catalyze such reaction very well [53]. Complexes **15** and **16** (Scheme 1.10) catalyse the oxidation of thioanisole using H_2O_2 as oxidant and gave 59 % conversion with 70 % ee towards sulfoxide [54, 55]. Introducing additional chirality (see **16** of Scheme 1.10) improved the conversion with 78 % ee. [56]. After encapsulating **15** in the super cages of zeoite-Y, it catalyzed the oxidation of thioanisole but the obtained sulfoxide was racemic and thus further analysis of the products is necessary [57, 58].



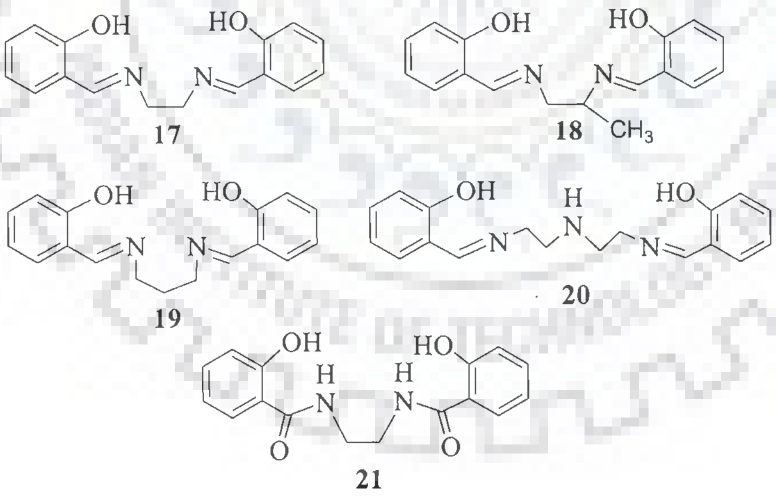
R = tert-butyl, NO_2

15 **16**

Scheme 1.10

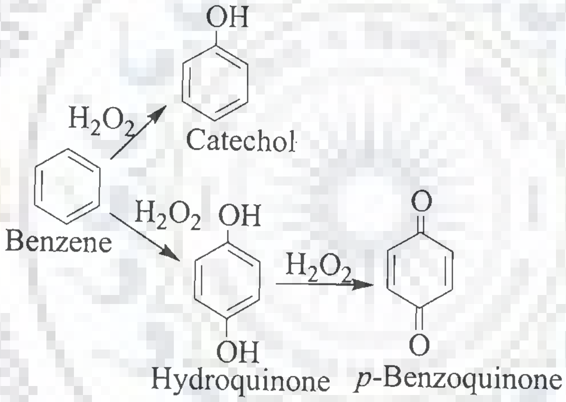
1.3.2.3. Schiff base complexes

Oxovanadium(IV) complexes of ligands H_2salen **(17)**, H_2sal-1,2-pn **(18)**, H_2sal-1,3-pn **(19)**, H_2saldien **(20)** and Hehybe **(21)** of Scheme 1.11 have been encapsulated in the cavity of zeolite-Y. These complexes catalyse the oxidation of phenol. The oxidation of phenol is one of the industrially important reactions. As the hydroxyl group on phenol is *ortho* and *para* directing, the catalytic oxidation of phenol usually gives two products catechol and hydroquinone. In some cases a further oxidation also occurs to give *p*-benzoquinone as shown in Scheme 1.12. Catechol has been used for pest control, pharmaceuticals, and flavors and aromas. Hydroquinone has mainly been used as photographic developer, polymerization inhibitor, antioxidant and intermediate for numerous dyes. Under the optimized conditions [VO(sal-1,3-pn)]-Y has shown ca. 34 % conversion while other two complexes, [VO(salen)]-Y and [VO(saldien)] register only 33 % conversion. As high as 90 % selectivity of catechol has been observed by later two complexes [59]. The [VO(salen)]-Y has also been used as active catalyst in the oxidation of toluene by H_2O_2 to produce benzaldehyde, benzylalcohol, *o*-cresol and *p*-cresol [60]. Oxidation of cyclohexane has also been carried out by similar complexes [61, 62].



Scheme 1.11

Zeolite encapsulated metal complexes prepared from other tetradentate Schiff base ligands also catalysed the oxidation of phenol using different oxidants. Thus, Cu(X-salen) [63], Mn(X-salen) [64] (X = H, Cl, Br or NO_2), have been used as catalysts. The oxidation products are mainly catechol and hydroquinone. In no cases the formation of 1,4-benzoquinone was detected. Oxidation of phenol has also been reported using copper(II), nickel(II), iron(III), chromium(III), bismuth(III) and zinc(II) complexes of ligands **17**, **18**, **19**, **20** and **21** encapsulated in zeolite-Y. In all cases conditions have been optimized considering effect of amount of catalyst, effect of substrate, H_2O_2 concentration and volume of solvent. It was observed that substrates to oxidant ratio of 1:2 worked nicely to effect maximum oxidation. The 3D model structure of $[Fe(hybe)(H_2O)_2]^+$ was created using CS Chem 3D ultra molecular modeling programme to show that xeolite-Y can accommodate the complex in its super cages without any strain; Figure 1.3 [37, 65-67].



Scheme 1.12. Various products of phenol oxidation.

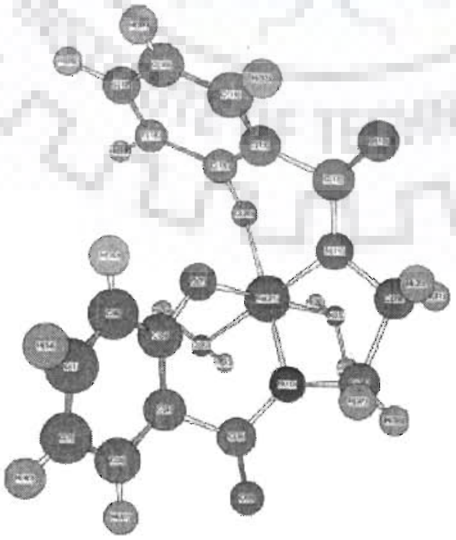
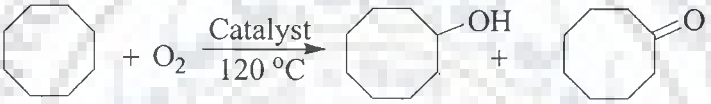


Figure 1.3. 3D model structure of $[Fe(hybe)(H_2O)_2]^+$.

Poltowicz *et al.* have encapsulated whole range of metallosalen complexes (e.g. [Fe(salen)], [Mn(salen)], [Cu(salen)] and Co(salen)]) in Na-X zeolite to study catalytic activity for the oxidation of cyclooctane. A model structure of entrapped [Co(salen)] complex published by them is reproduced in Figure 1.4. Two oxidation products, cyclooctanone and cyclooctanol have been obtained on oxidation of cyclooctane; Scheme 1.13. Except [Ni(salen)]-X, the catalytic activities of these complexes dropped to half on encapsulation than observed by respective neat complexes. The changes in the redox potential of the metal ion in complexes and constraints in the formation of the intermediate complex have been suggested to be possible reason for the poor catalytic activity [68].



Scheme 1.13

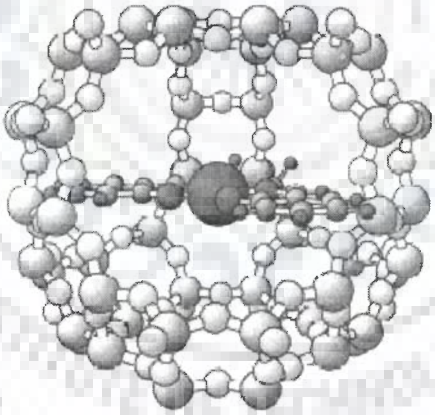


Figure 1.4. Model structure of entrapped [Co(salen)] complex in zeolite-X.

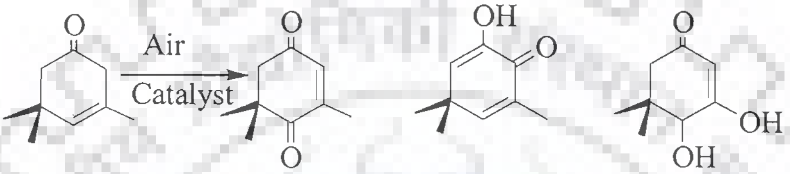
Ratnasamy *et al.* have isolated copper(II) and manganese(III) complexes of salen derivatives encapsulated in the cavity of zeolite-X and zeolite-Y by zeolite synthesis method. The structures of the complexes have been characterized by FTIR, UV-visible and EPR spectroscopic techniques, XRD, SEM, thermal and elemental analysis, as well as nitrogen absorption and cyclic voltametric studies. Cyclic voltammetric studies for manganese(III) complexes indicate that the zeolite matrix facilitates the reduction of Mn(III) to Mn(II) and this suggests that zeolite behaves like electron-withdrawing substituent. The oxidation of styrene under aerobic conditions using tert-butylhydroperoxide gave benzaldehyde, styrene and phenylacetaldehyde. The catalytic efficiency of these encapsulated complexes were much higher than that of the neat complexes. Electron withdrawing substituents such as -Cl, -Br, -NO_2 on the aromatic ring enhances the rate of oxidation [69, 70].

These complexes also catalyse the oxidation of phenol and p-xylene. The aerobic oxidation of p-xylene in the absence of added hydrogen promoters and using *tert*-butyl hydrpperoxide as the initiator and Mn(X-sal-1,3-pn)Cl]-X and [Mn(sal-dach)Cl]-X H_2sal-dach = Schiff derived from salicylaldehyde and 1,2-diaminocyclohexane) at low temperature showed as high as 60 % conversion. Again conversion increased in presence of electron withdrawing group on the aromatic ring [71, 72].

Manganese(III) and nickel(II) complexes of H_2salen have also been used as catalyst for the epoxidation of cyclohexene, cyclooctene and 1-hexene using NaOCl and $KHSO_5$ as terminal oxidants. Selectivity in the epoxidation of linear olefins is possibly the result of small pore size of the zeolite host which governs the molecular sieving and orientation properties [73].

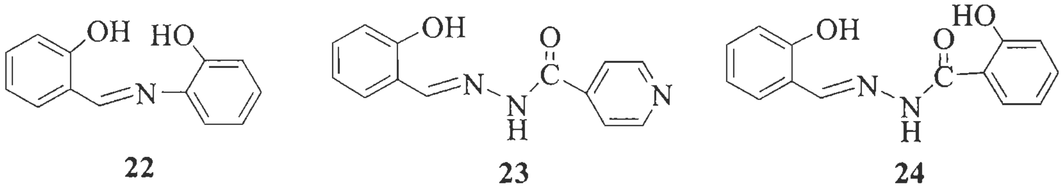
Complex, $[Mn(salen)]^+$ encapsulated in zeolite-Y has been used for the asymmetric epoxidation of *cis*-β-methylstyrene with sodium hypochlorite [74]. Other similar complexes have also been used for the epoxidation of various types of alkenes, arenes and cycloalkenes [36, 75, 76]. The $[Mn(salen)]^+$-Y has been reported to be steriospecific in the epoxidation of *trans* stilbene as well as active for the epoxidation of *cis*-substituted aryl alkenes [77, 78].

Complexes, [Co(salophen)]-Y and related derivatives have been used as catalyst for the oxidation of β-isophorone (βIP) to keto isophorone (KIP) along with other minor products using air as an oxidant at ambient conditions of temperature and pressure; Scheme 1.14. The activities of these encapsulated catalysts was in the order: [Co(Cl-salophen)]-Y > [Co(Br-salophen)]-Y > [Co(NO_2-salophen)]-Y > [Co(salophen)]-Y. The selectivity for KIP was >95 % at βIP conversion of ~30 % in the beginning which slowly decreased with time to ~60 % selectivity at higher conversion (>95 %) of βIP [79]. Ruthenium(III) and Cobalt(II) complexes of H_2X-salophen (X = Cl, Br and NO_2) encapsulated in zeolite-Y has been found to be efficient for the allylic oxidation of α-pinene [80].



Scheme 1.14. Reaction scheme of oxidation of β-isophorone

Complexes $NH_4[VO_2(sal\text{-}inh)(H_2O)]$-Y ($H_2$sal-inh = Schiff base derived from salicylaldehyde and iso nicotinic acid hydrazide, **23**) and $NH_4[VO_2(sal\text{-}oap)(H_2O)]$-Y ($H_2$sal-inh = Schiff base derived from salicylaldehyde and *o*-aminophenol, **22**); Scheme 1.15) encapsulated in zeolite-Y catalyze the oxidative bromination of salicylaldehyde to give 5-bromosalicylaldehyde with 90 % selectivity. These complexes have been encapsulated by reacting pre-exchanged ammonium vanadate with zeolite-Y with sodium salt of ligand in aqueous solution followed by adjusting pH to ca. 7.5 [81]. Complexes $NH_4[VO_2(sal\text{-}inh)(H_2O)]$-Y and $NH_4[VO_2(sal\text{-}oap)(H_2O)]$-Y also catalyze the oxidation of phenol to give catechol and hydroquinone with good selectivity towards catechol [82]. Dioxomolybdenum(VI) complex of similar ligand H_2sal-shz **(24)** catalyze aerial oxidation of cyclooctene [83].



Scheme 1.15

The manganese(III), iron(III) and cobalt(III) complexes of Schiff base derived from *m*-nitrobenzaldehyde and 2,6-diaminopyridine encapsulated in Na-Y zeolite whose cage size was extended have been isolated and characterized. These catalysts have been used for the aerobic oxidation of 1-octene. The effect of temperature, organic acid or base, and the amount of catalyst have been considered to optimize the reaction conditions to give high activity and selectivity of the substrate and products [84].

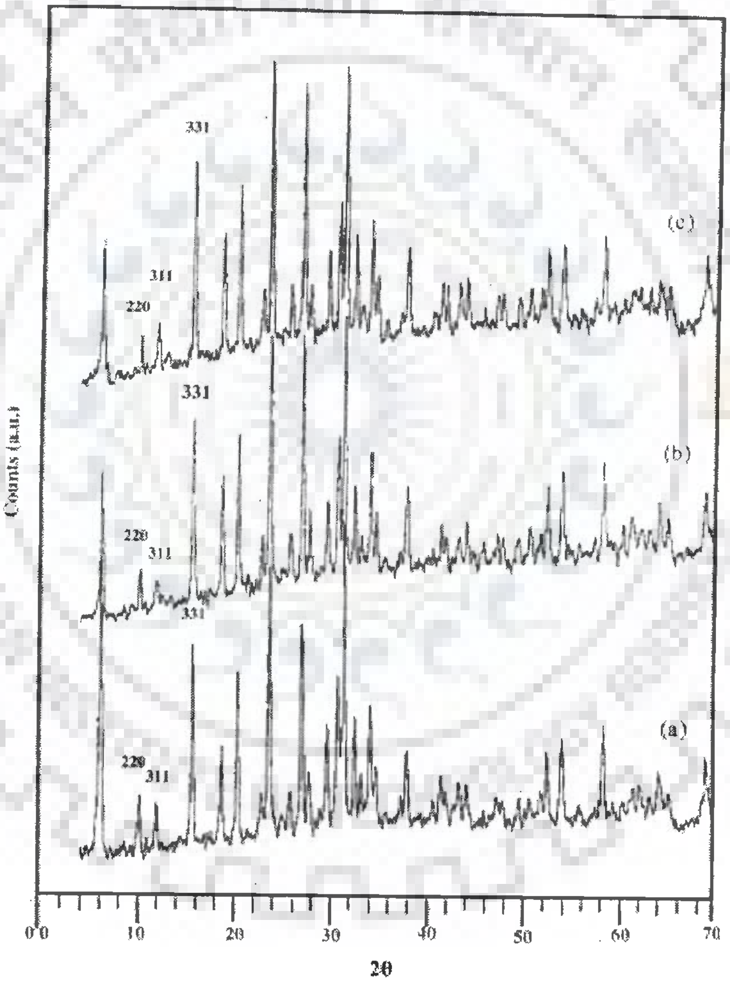


Figure 1.5. X-ray powder diffraction pattern of (a) Na-Y, (b) Cu(II)-Y and (c) Cu(sal-amba)]-Y.

Copper(II)-salicylaldehyde-p-aminobenzoic complex, [Cu_2(sal-amba)$(H_2O)_5$]-Y has been encapsulated in zeolite-Y. The EPR spectrum of the encapsulated complex suggests the existence of binuclear complex with coordination of nitrogen and oxygen atoms (from carboxylic, phenolic and water). Its encapsulation has also been confirmed by X-ray diffraction study, Figure. 1.5. This complex adsorbs CO and form Cu(I)-CO species which is stable to thermal evacuation [85].

Not only oxidation, zeolite encapsulated complexes e.g. [Pd(salen)] and [Ni(salen)] encapsulated in zeolite X and Y have been used for the hydrogenation of olefins [86].

1.3.2.4. Metallophthalocyanines, metalloporphyrins and macrocyclic complexes

Metal phthalocyanines encapsulated in zeolite-X, zeolite-Y (MPc-Y) and ZSM-5 prepared by *in situ* ligand synthesis have been studied for the oxidation of phenol by H_2O_2 . It was observed that metal ion of the catalyst influences both activity and selectivity of the reaction. This difference has been explained on the basis of the H_2O_2 decomposition and hydroxyl radical formation ability. Metal with higher redox potential tends to decompose H_2O_2 more easily as they switch easily between two valencies as shown below; Scheme 1.16. [87-92].

$$M^{[n^+]} + H_2O_2 \longrightarrow H_2O_2\,M^{[(n-1)^+]} + HOO^{\cdot} + H^+ \text{ (rate } + k_d)$$

$$M^{[(n-1)^+]} + H_2O_2 \longrightarrow M^{[n^+]}\,OH + {}^{\cdot}OH$$

$$OH^{\cdot} + H_2O_2 \longrightarrow HOO^{\cdot} + H_2O$$

$$2HOO^{\cdot} \longrightarrow O_2 + OH^{\cdot}$$

Scheme 1.16: Reaction mechanism of phenol hydroxylation.

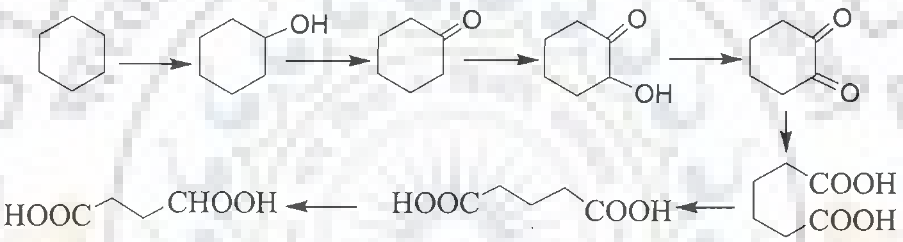
Raja and Ratnasamy [93] have reported the oxyhalogenations of benzene, toluene, phenol, aniline, anisole and resorcinol using phthalocyanines of Cu, Fe and Co encapsulated in zeolites X, Y and L. Both H_2O_2 and O_2 have been used as oxidants. Initiater *tert*-butyl hydroperoxide (TBHP 70% aqueous solution) has been used during oxyhalogenation reactions by molecular O_2. Oxidized products, benzaldehyde and benzyl alcohol have also been observed along with oxyhalogenated products in case of toluene. Oxidation of phenol and aniline always gave mono-, di- and tri-haloproducts. The oxyhalogenation of benzene resulted only monohalobenzene when molecular oxygen (with or without TBHP as initiator) was used as oxidant, though, percent conversion was very low. Use of H_2O_2 as oxidant gave better conversion but formation of all three monohalo-, dihalo- and trihalobenzenes were observed. Some of these results are summarized in Table 1.2.

Table 1.2. Oxyhalogenation of benzene over $CuCl_{16}Pc$-Na-X [a] [93]

Oxidant	Initiator	Halide	Conversion (%)	Halogenated products (wt %)		
				Mono-	Di-	Tri-
H_2O_2	--	KCl	9.7	47.5	37	15.5
H_2O_2	--	KBr	11.5	58	34	8
O_2	--	KCl	3.2	100	--	--
O_2	--	KBr	4.1	100	--	--
O_2	TBHP	KCl	5.5	100	--	--
O_2	TBHP	KBr	6.2	100	--	--

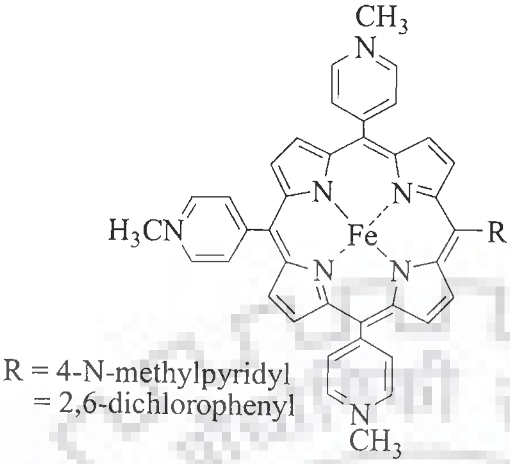
[a] Wt. % copper in the form of hexa decachloro copper phthalocyanine complex encapsulated in the super cages of the faujasite structure

Direct conversion of methane to a mixture of methanol and formaldehyde, and propane to a mixture of isopropanol and acetone have been achieved at ambient conditions with high activity and selectivity using phthalocyanines complexes of iron cobalt and nickel encapsulated in zeolites as catalysts and O_2/ *tert*-butyl hydroperoxide as oxidant [94, 95]. Metal phthalocyanines encapsulated in zeolite have also been used for the oxidation of hydrocarbons [96]. The oxidation of olefins like cyclohexene and 1-hexene were carried out with iodosylbenzene and *tert*-butyl hydroperoxide as oxidant in chloroform using CoPc-Y. It was observed that the encapsulated phthalocyanine was active even after 20 h of reaction [97]. Oxidation of cyclohexane catalysed by iron phthalocyanine encapsulated in Y-zeolites using *tert*-butyl hydroperoxide as oxygen donor gave cyclohexanol and cyclohexanone [98, 99]. Adipic acid, succinic acid, glutaric acid, valeraldehyde and valeric acid have also been identified in some cases. The reaction sequence for the oxidation of cyclohexane is given below in Scheme1.17. Biproducts like succinic acid and glutaric acids did not form when acetonitrile was used as the solvent. Effect of solvent in the oxidation of cyclohexane and cyclohexanone using *t*-BOOH catalysed by FePc/NaY have been studied by Jacobs *et al.* [100]. The bulky groups present on the alkyl hydroperoxide influences the rate of oxidation in the order: cyclohexyl > *t*-butyl > cumyl.



Scheme 1.17. Sequence of oxidation of cyclohexane

Iron(III) 5, 10, 15, 20-tetrakis(4-N-methylpyridyl)porphyrin (FeP**1**) (**25**, X = 4-N-methylpyridyl) and iron(III) 5-mono(2,6-dichlorophenyl)-10, 15, 20-tris(4-N-methylpyridyl)porphyrin (FeP**2**) (**25**, X = 2,6-dichlorophenyl) have been encapsulated in NaX by zeolite synthesis method; Scheme 1.18. FeP**1**NaX and FeP**2**NaX efficiently catalyzed the oxidation of (Z)-cyclooctane by iodosylbenzene (PhIO) to give cis-epoxycyclooctane in 85 % and 95 % yield. Hydroxylation of admantane catalyzed by these catalysts showed a preferable alkane oxidation at the tertiary C – H bond, indicating a hydrogen abstraction through the $Fe^{IV}O(P)$ species in the initial step. A maximum of 52 % with FeP**1**NaX and 45 % with FeP**2**NaX conversion has been achieved where the ratio of 1-admantanol/ 2-admantanol was 20:1 and 11:1, respectively [101]. Oxidations of aliphatic and aromatic hydrocarbons have also been achieved using metalloporphyrins [102, 103].

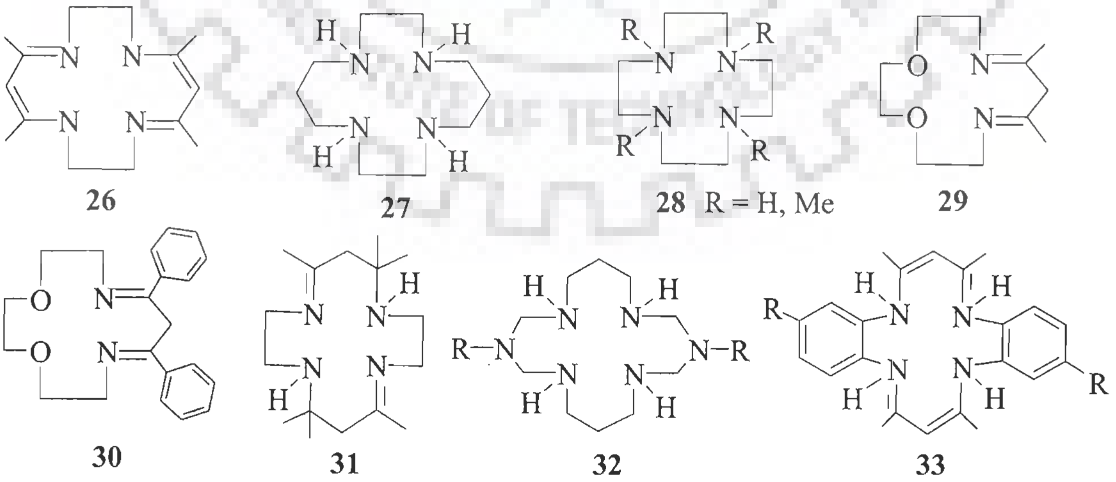


R = 4-N-methylpyridyl
= 2,6-dichlorophenyl

25

Scheme 1.18

Macrocyclic complexes have also been encapsulated in the cavity of zeolites. Medina *et al.* have encapsulated iron complex of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene **(26)** by flexible ligand method; Scheme 1.19 [104]. The oxidation of cyclohexene using iodosylbenzene as oxygen donor gave 2-cyclohexene-1-ol, 2-cyclohexene-1-one and cyclohexene eopxide; Scheme 1.20. Similarly different metal complexes **(27)** to **(33)** presented in Scheme 1.19 have been encapsulated and studied for various oxidation reactions [105-110].

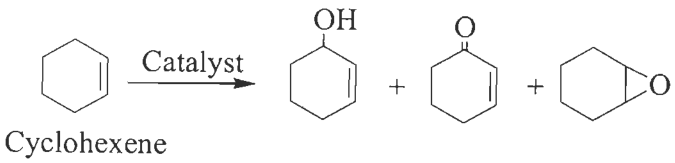


26 **27** **28** R = H, Me **29**

30 **31** **32** **33**

R = H, Me, Et, Bu, Benzyl R = H, Me, Cl, NO_2

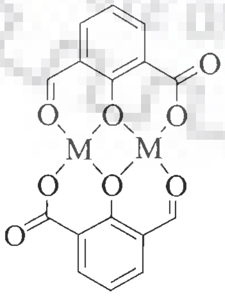
Scheme 1.20.



Scheme 1.19

1.3.2.5. Complexes with other type of ligands

Binuclear copper(II), nickel(II) and cobalt(II) complexes of 3-formylsalicyclic (H_2fsal) **(34)** have been encapsulated in zeolite-Y for the oxidation of benzyl alcohol and ethylbenzene; Scheme 1.21. It has been proposed that an intermediate binuclear oxo complexes form during reaction which finally transfers oxygen to the substrate to give product. Their catalytic potential vary in the order: $[\{Cu(fsal)\}_2]$-Y > $[\{Co(fsal)\}_2]$-Y > $[\{Ni(fsal)\}_2]$-Y [111]. Partial oxidation of these substrates has also been catalyzed by zeolite-Y encapsulated copper(II), nickel(II) and cobalt(II) complexes of dimethylglyoxime [112]. The same group have also reported the catalytic oxidation of ascorbic acid by atmospheric oxygen using $[Cu(dmpz)_2]$-Y (Hdmpz = 3,5-dimethyl-1H- pyrazole) as catalyst. The oxidation of ascorbic acid to dehydroascorbic acid was monitored spectroscopically at 245 nm after exposing deoxygenated methanolic solution of ascorbic acid in air in the presence of catalyst. It has been proposed that oxidation proceeds through Cu(I)-ascorbate intermediate [113]. The catalytic reduction of oxygen (industrially known as deoxo reaction) by copper(II) complexes of embelin and 2-aminobenzimidazole encapsulated in the cavity of zeolite-Y was found to be enhanced with respect to that reported for simple complexes [114].



34

Scheme 1.21. Dinuclear structure of $[\{M(fsal)\}_2]$ complexes; M = Cu(II), Ni(II), Co(II).

Jacobs *et al.* have reported *cis*-$[Mn(bipy)_2]^{2+}$ encapsulated in zeolite X and Y and used them for the oxidation of a series of alkenes and cycloalkenes with H_2O_2 as oxidant. The percent conversion and selectivity of various products at room temperature are summarized in Table 1.3. The catalytic epoxidation of cycloalkene is followed by acid-catalyzed ring opening. Thus, adipic acid from cyclohexene has also been obtained [35]. Similar iron(II) and manganese(II) complexes of 2,2′-dipyridyl have also been isolated by Niassary *et al.* for the oxidation of cyclic ethers, such as, tetrahydrofuran, tetrahydropyron, 2,3-dihydropyron and 1,4-dioxane using H_2O_2 and TBHP as oxidant. Mainly cyclic ether-2-ols and cyclic ether-2-ones have been obtained. Minor product, 2,3-dihydro cyclic ether has also been detected in some cases [115].

Table 1.3. Oxidation of alkenes on *cis*-$[Mn(bpy)_2]^{+2}$ in zeolite X and Y at 293 K [35]

S. No.	Catalyst	Substrate	Time (h)	Conv. (%)	Selectivity (%)		
					Oxide	Diol	Diacid
1	$[Mn(bpy)_2]$-X	1-Hexene	4	2	81	14	--
2	$[Mn(bpy)_2]$-Y	1-Hexene	18	20	50	40	--
3	$[Mn(bpy)_2]$-X	Cyclohexene	4	41	62	32	--
4	$[Mn(bpy)_2]$-Y	Cyclohexene	18	62	6	79	--
5	$[Mn(bpy)_2]$-Y	Cyclohexene	40	100	--	--	80
6	$[Mn(bpy)_2]$-X	1-Dodecene	4	11	74	22	--
7	$[Mn(bpy)_2]$-Y	1-Dodecene	18	20	10	88	--
8	$[Mn(bpy)_2]$-X	Cyclododecene	4	38	78	22	--
9	$[Mn(bpy)_2]$-Y	Cyclododecene	18	56	4	87	--
10	$[Mn(bpy)_2]$-Y	Cyclododecene	40	100	--	--	84

Oxovanadium(IV) picolinate, $[VO(pic)_2]$ encapsulated in zeolite-Y has been studied for the oxidation of cyclohexane, isopropanol and benzene using H_2O_2 as an oxidant. Leaching of $[VO(pic)_2]$ has, however, been noticed in the presence of H_2O_2

[116]. The monopero oxovanadium(V) monopicolinate complex has been isolated by the treatment of encapsulated complex with urea hydrogen peroxide in acetonitrile, the formation of which has been confirmed by UV-visible, Raman and XAFS studies. This novel catalyst retains the solution like activities in aliphatic and aromatic hydrocarbon oxidations as well as in alcohol oxidation [117].

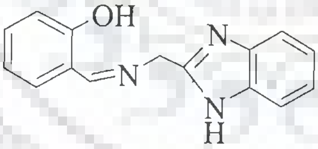
Ratnasamy *et al.* have prepared dimeric [Cu(CH_3COO)$_2$.H_2O] in the cavity of zeolite-Y. The convincing proofs of dimer comes from EPR study, which gives 7-line hyperfine structure due to the two Cu(II) nuclei. The activity of the complex has been evaluated in the aerial oxidation of phenols, which is in natural system catalyzed by the dicopper enzyme tyrosinase [118].

1.4. OBJECTIVE OF THE PRESENT THESIS

It is evident from the review of the literature that zeolite encapsulated metal complexes have provided opportunities to develop catalytic system for various industrial processes. Particularly, oxidation reactions catalyzed by these specialized class of immobilized complexes are well documented. However, in most cases optimization of the reaction conditions to effect maximum efficiency of the catalysts has not been set out. It was, therefore, reasonable to under take systematic study on the synthesis and characterization of new zeolite-Y encapsulated catalysts and to explore their catalytic potential for the oxidation of organic substrates under optimized reaction conditions.

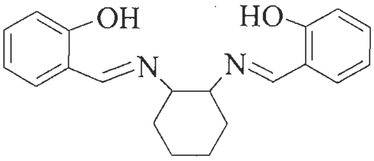
The present study is aimed to describe the syntheses of zeolite-Y encapsulated metal complexes with the following ligands:

(i) Monobasic tridentate ONN donor Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole (Hsal-ambmz, **I**).



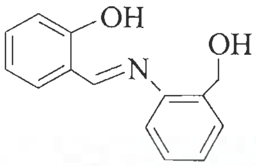
I: Hsal-ambmz

(ii) Dibasic tetradentate ONNO donor Schiff base derived from salicylaldehyde and 1,2-diaminocyclohexane (H_2sal-dach, **II**).



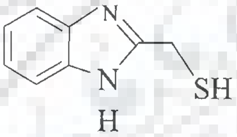
II: H_2sal-dach

(iii) Dibasic tridentate ONO donor Schiff base derived from salicylaldehyde and *o*-aminomethylbenzylalcohol (H_2sal-oaba, **III**).



III: H_2sal-oaba

(iv) Monobasic bidentate NS donor ligand 2-mercaptomethylbenzimidazole (Htbmz, **IV**).



IV: Htbmz

Synthesized complexes have been characterized by chemical, spectral (IR and electronic) and thermal studies, XRD patterns and scanning electron micrographs. Catalytic potential of these complexes have been explored for the following reactions

(i) Oxidation of phenol
(ii) Oxidation of styrene
(iii) Oxidation of cyclohexene
(iv) Oxidation of cyclohexane
(v) Oxidation of methyl phenyl sulfide
(vi) Oxidation of diphenyl sulfide

Reaction conditions for all these catalytic reactions have been optimized to get best performance of the catalysts.

CHAPTER-2

Oxidation of phenol, styrene and methyl phenyl sulfide with H_2O_2 catalyzed by dioxovanadium(V) and copper(II) complexes of 2-aminomethylbenzimidazole based ligand encapsulated in zeolite-Y

2.1. INTRODUCTION

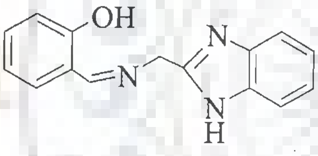
Heterogeneous catalysts have played a key role in the development of industrial processes for chemical industry. There are three general methods to heterogenize homogeneous catalysts: i) by polymerization of homogeneous catalyst it self [119-123] and thus making them insoluble in solvents, ii) by immobilization of homogeneous catalyst through covalent bonding with polymeric materials [124-127] or materials like functionalized MCM-41, SBA-15 etc. [13, 128] and iii) by encapsulating them in the nano cavity of e.g. zeolites [64, 129-132]. Latter two methods provide additional characteristic properties such as activity, selectivity, thermal stability and reusability of the catalysts. In recent years zeolite encapsulated metal complexes (ZEMC) have provided the opportunity to develop catalytic process for the selective oxidation, alkylation, dehydrogenation, cyclization, amination, acylation, isomerization and rearrangement of various substrates and are able to produce intermediates as well as most industrial products [64, 129-131].

Liquid phase hydroxylation of phenol, by molecular oxygen and H_2O_2, is industrially important reaction. Several heterogeneous catalytic methods have been developed for the oxidation of phenol and wide range of products selectivity has been reported [133-138]. The catalysts based on zeolite encapsulated metal complexes have played excellent role in this regard [21, 89, 139]. We have reported oxidation of phenol using salen (H_2salen = N,N′-bis(salicylidene)-1,2-diaminoethane) based transition metal complexes and have shown that selectivity towards the formation of catechol was ca. 90 % with [VO(salen)] encapsulated in zeolite-Y [59].

Styrene epoxide, an important intermediate for the manufacture of perfumery chemical phenylethyl alcohol, is oxidation product of styrene. Homogeneous and heterogeneous catalysts have been used for the epoxidation of styrene [35, 140-144].

In this work, we have encapsulated copper(II) and dioxovanadium(V) complexes of Schiff bases derived from salicylaldehyde and 2-aminomethylbenzimidazole (Hsal-ambmz, **2.I,** Scheme 2.1) in the super cages of zeolite-Y and characterised. Their catalytic activities have been tested for the liquid phase oxidation of phenol and styrene.

Enzyme vanadate-dependent haloperoxidases catalyse the oxidation of sulfides (thioethers) to sulfoxides and further to sulfones [145]. Vanadium complexes are known to mimic sulfoxidases activity [144, 146, 147]. We have, therefore, tested sulfoxidases activity also with encapsulated vanadium complex in question.



2.I: Hsal-ambmz

Scheme 2.1

2.2. EXPERIMENTAL

2.2.1. Materials

Analytical reagent grade cupric nitrate, cupric chloride, 30 % aqueous H_2O_2, salicylaldehyde (sal), *o*-phenylenediamine were obtained from E. Merck, India. Vanadyl sulfate penta hydrate, glycine and phenol were obtained from Loba Chemie, India. Methyl phenyl sulfide obtained from Alfa Aeaser, U.S.A. and styrene from Acros Organics. New Jersey, U.S.A. were used as such. Zeolite-Y (Si/Al = ca.10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were of AR grade. 2-Aminomethylbenzimidazole dihydrochloride (ambmz·2HCl) was prepared following the procedure reported in the literature [148].

2.2.2. Physical methods and analysis

Copper and vanadium were analyzed using inductively coupled plasma (ICP; Labtam 8440 plasmalab) after leaching the metal ions with conc. nitric acid and diluting with distilled water (for copper) or with very dilute aqueous KOH solution (for vanadium) to specific volume in volumetric flask. Electronic spectra were recorded in Nujol using Shimadzu 1601 UV-vis spectrophotometer by layering the mull of the sample to inside of one of the cuvettes while keeping the other one layered with Nujol as reference. Spectra of neat complexes were recorded in methanol. IR spectra were recorded as KBr pellet on a Nicolet NEXUS Aligent 1100 series FT-IR spectrometer after grinding the sample with KBr. Thermogravimetric analyses of pure as well as encapsulated complexes were carried out using TG Stanton Redcroft STA 780. X-ray powder diffractograms of solid catalysts were recorded using a Bruker AXS D8 Advance X-ray powder diffractometer with a Cu-Kα target. All catalyzed reaction products were analysed using Thermoelectron gas-chromatograph having HP-1 capillary column (30m × 0.25 mm × 0.25 μm) and FID detector. Scanning electron micrographs (SEMs) of catalysts were recorded on a Leo instrument model 435VP. The samples were dusted on alumina and coated with thin film of gold to prevent surface changing and to protect the surface material from thermal damage by electron beam. In all analysis, a uniform thickness of about 0.1 mm was maintained.

2.2.3. Preparations

2.2.3.1. Preparation of Hsal-ambmz

Ligand Hsal-ambmz was prepared as reported previously [144]. An aqueous solution of ambmz·2HCl (1.10 g, 5 mmol in 15 ml) was neutralized by adding aqueous K_2CO_3 solution (0.83 g, 6 mmol). A methanolic solution of salicyaldehyde (0.61g, 5 mmol in 10 ml) was added drop-wise to the above solution with stirring within 1 h. During this period, yellow solid slowly separated out which was filtered, washed thoroughly with water followed by petroleum ether and dried in vacuo at room temperature. Finally, it was recrystallized from minimum amount of acetonitrile. Yield: 70%. Anal. found: C, 71.32; H, 5.37; N, 16.52 %. Calcd. for

$C_{15}H_{13}N_3O$ (251.29): C, 71.70; H, 5.21; N, 16.72 %. ^{1}H NMR (DMSO-d_6, δ/ppm):12.90(b, 1H, -OH); 8.95(s, 1H, -CH=N-); 6.98(d, 3H), 7.41(m, 4H), 7.67(d, 1H) (aromatic); 5.05(s, 2H, $-CH_2-$).

2.2.3.2. Preparation of OV(IV)-Y (oxovanadium exchanged zeolite)

A filtered solution of $VOSO_4.5H_2O$ (3.0 g, 12 mmol) dissolved in 50 ml of distilled water was added to a suspension of Na-Y zeolite (5.0 g) in 300 ml of distilled water and the reaction mixture was heated at 90 °C with stirring for 24 h. The bluish solid was filtered, washed with hot distilled water until filtrate was free from any vanadyl ion content, and dried at 150 °C for 24h.

2.2.3.3. Preparation of Cu(II)-Y (copper exchanged zeolite)

Cu(II)-Y was prepared following essentially the same procedure out lined for OV(IV)-Y replacing $VOSO_4$ by $Cu(NO_3)_2$.

2.2.3.4. Preparation of [V^VO_2(sal-ambmz)]-Y (2.1)

A mixture of OV-Y (1.0 g) and Hsal-ambmz (2.5 g) was mixed in 100 ml of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was suction filtered and then extracted with methanol using Soxhlet extractor until the complex was free from unreacted ligand. The solid was further suspended in methanol and oxidized by passing air while stirring at room temperature for 24 h. After filtering, the uncomplexed vanadium(IV/V) ions present in the zeolite was removed by stirring with aqueous 0.0.1 M NaCl solution for 8 h. Finally the resulting solid was washed with water until free from chloride ions and dried at 120 °C for several hours to constant weight.

2.2.3.5. Preparation of [Cu^{II}(sal-ambmz)Cl]-Y(2.2)

A methanolic solution of Hsal-ambmz (2.5 g in 50 ml) was added to Cu-Y suspended in 50 ml of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was filtered off and extracted with methanol till the complex was free from unreacted Hsal-ambmz. The uncomplexed Cu(II) ion present in the zeolite-Y was removed by stirring with aqueous 0.01 M NaCl solution for 8 h. It was filtered, washed with distilled water till no trace of chloride ion and dried at 120 °C for several hours to constant weight.

2.2.3.6. Preparation of [V^VO_2(sal-ambmz)](2.3)

This complex was prepared following the procedure reported in the literature [31]. Yield: 75 %. Anal. found: C, 53.76; H, 3.76; N, 12.42 %. Calcd. for $C_{15}H_{12}N_3O_3V$ (333.22): C, 54.07; H, 3.63; N, 12.61 %. ^1H NMR (DMSO-d_6, δ/ppm): 9.10(s, 1H, -CH=N-); 6.86(d, 3H), 7.38(s, 1H), 7.50(t, 1H), 7.60(d, 1H), 7.66(d, 1H), 8.10(d, 1H) (aromatic); 5.52(s, 2H, -CH_2-).

2.2.3.7. Preparation of [Cu^{II}(sal-ambmz)Cl](2.4)

A solution of $CuCl_2.2H_2O$ (0.852 g, 5 mmol) dissolved in methanol (20 ml) was added to a hot solution of Hsal-ambmz (1.26 g, 5 mmol) in 30 ml of methanol, and the reaction mixture was refluxed on a water bath for 5 h. Green solid of [Cu(sal-ambmz)Cl] slowly separated out within a few hours period on cooling the solution to ambient temperature. This was filtered off, washed with methanol and dried. Yield: 68 % Anal. found: C, 50.72; H, 3.92; N, 12.23 %. Calcd. for $C_{15}H_{12}N_3OClV$ (368.33): C, 51.38; H, 3.71; N, 11.99 %.

2.2.4. Catalytic activity studies

2.2.4.1. Oxidation of phenol

The catalytic hydroxylation of phenol was carried out in a 50 ml flask fitted with a water circulated condenser. In a typical reaction, 30 % aqueous H_2O_2 (17.01 g, 0.15 mol) and phenol (4.7 g, 0.05 mol) were mixed in 2 ml of MeCN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. An appropriate catalyst (0.025 g) was added to the reaction mixture and the reaction was considered to begin. During the reaction, the products were analysed by withdrawing small aliquots after specific interval of time using a gas chromatograph, and confirming the identity by GC-MS. The effects of various parameters, such as amounts of oxidant, and catalyst as well as the temperature of the reaction were studied in order to see their effect on the conversion and selectivity of the reaction products.

2.2.4.2. Oxidation of styrene

Styrene (0.50 g, 0.005 mol), aqueous 30 % H_2O_2 (1.70 g, 0.015 mol) and catalyst (0.015 g) were taken in 10 ml of CH_3CN and the reaction was carried out at 75 °C. The progress of the reaction was monitored as mentioned above and identity of various products confirmed by GC-MS.

2.2.4.3. Oxidation of methyl phenyl sulfide

Methyl phenyl sulfide (0.62 g, 0.005 mol) was dissolved in 20 ml of acetonitrile. After addition of H_2O_2 (0.57, 0.005 mmol) and catalyst (0.005 g), the reaction mixture was stirred at room temperature for 2 h. During the reaction, the reaction products formed were analysed using gas chromatograph by withdrawing small aliquots after specific interval of time. The identities of the products were confirmed by GC-MS.

2.3. RESULTS AND DISCUSSION

2.3.1. Characterization of catalysts

Synthesis of metal complexes encapsulated in the nano-cavity of zeolite-Y involves two steps: (i) exchange of VO(IV) and Cu(II) ions with NaY in aqueous solution and (ii) reaction of metal exchanged zeolites i.e. OV(IV)-Y and Cu(II)-Y with excess Hsal-ambmz in methanol where ligand slowly enters into the cavity of zeolite-Y due to its flexible nature and interacts with metal ions. This method has been described as flexible ligand method [64, 21]. Soxhlet extraction using methanol finally purified the impure complexes. In case of vanadium complex, initially formed oxovanadium(IV) species slowly oxidizes by air in solution to give dioxovanadium(V) complex [VO_2(sal-ambmz)]. The remaining uncomplexed metal ions in zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. As one extra anionic ligand would be required to balance the over all charges on the Cu(II), Cl^- of NaCl used during exchanged process fulfills this requirement. Thus, the formula of copper(II) complex may be written as [Cu(sal-ambmz)(Cl)]-Y. The percentage of metal contents determined before and after encapsulation by inductively coupled plasma (ICP; Labtam 8440 plasma lab), along with their expected formula and color are presented in Table 2.1. As crude mass was extracted with methanol, the metal ion content found after encapsulation is only due to the presence of metal complexes in the super cages of the zeolite-Y. The molecular formula of the complexes are based on the neat complexes [VO_2(sal-ambmz)] and [Cu(sal-ambmz)Cl] that have also been prepared and characterised.

Table 2.1. Chemical composition, physical and analytical data

No.	Catalyst	Color	Metal content (wt %)
1	OV-Y	Light green	4.58
2	[VO_2(sal-ambmz)]-Y	Light cream	1.82
3	Cu-Y	Pale blue-green	7.60
4	[Cu(sal-ambmz)Cl]-Y	Pale brown	2.57

2.3.2. 3D Molecular structure

A C.S. Chem Ultra molecular modeling and analysis programme [149] was used to create three-dimensional model structure for [VO_2(sal-ambmz)]. Figure 2.1 presents the molecular structure, and the selected bond lengths and bond angles are given along with the figure's caption. Complex [VO_2(sal-ambmz)] represents the distorted trigonal pyramid where phenolate-O (O9) and the benzimidazole-N (N21) are in the axial position ($\angle$O9 – V12 – N21 = 168.098 Å). The azomethine-N and the two doubly bonded oxygen atoms are in the trigonal plane. Similar structure for a closely related complex [VO_2(sal-aebmz)] (Hsal-aebmz = Schiff base derived from salicylaldehyde and 2-aminoethylbenzimidazole) has been structurally characterized by single crystal X-ray study [144].

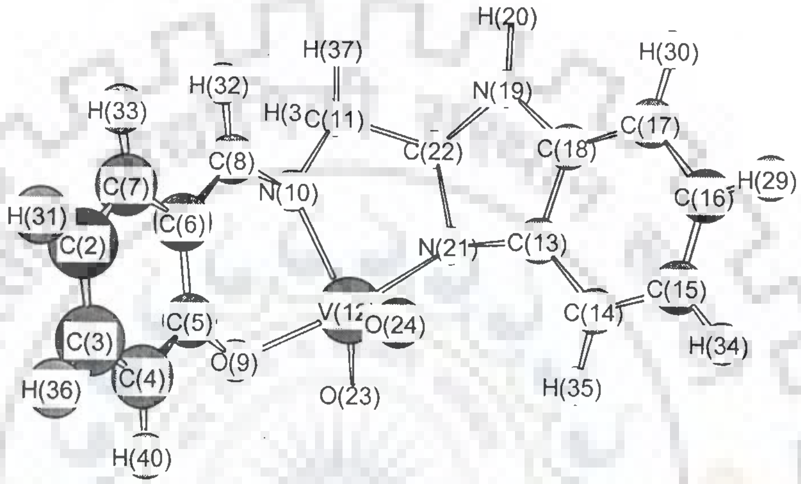


Figure 2.1. 3D model structure of [VO_2(sal-ambmz)]. Bond length (Å): V–O(9), 1.873; V–N(10), 1.910; V–N(21), 1.918; V–O(23), 1.868; V–O(24), 1.865. Bond angle (°): O(9)–V–N(21), 168.098; O(9)–V–N(10), 88.017; N(10)–V–N(21), 84.702; N(10)–V–O(23), 123.633; N(10)–V–O(24), 107.407; N(21)–V–O(23), 87.666; N(21)–V–O(24), 97.091; O(23)–V–O(24), 128.959.

Most [Cu(ONN)X] (where ONN = coordinating atoms of monobasic ligands, X = Cl^-, Br^-, N_3^-, etc.) type complexes exist as dimmer / polymer where each unit has square pyramidal structure through bridging of X^- [150-152]. Complex [Cu(sal-ambmz)Cl] may also exist as dimmer / polymer. However, such dimeric / polymeric structure will not be possible for the complex [Cu(sal-ambmz)Cl] encapsulated in zeolite-Y due to space constraint. As spectral patterns of neat as well as encapsulated complexes (vide infra) are same, a square planar structure may also be suggested for encapsulated complexes and this is possible only on additional coordination of e.g. water with Cu(II). Therefore, no attempt has been made to give three dimensional model structure for the neat complex [Cu(sal-ambmz)Cl].

2.3.3. Scanning electron micrograph studies

The scanning electron micrographs (SEM) of the metal exchanged zeolite and their respective encapsulated complexes indicate the presence of well defined crystals free from any shadow of the metal ions or complexes present on their external surface. The representative micrographs of OV(IV)-Y and (b) [VO_2(sal-ambmz)]-Y are presented in Figure 2.2.

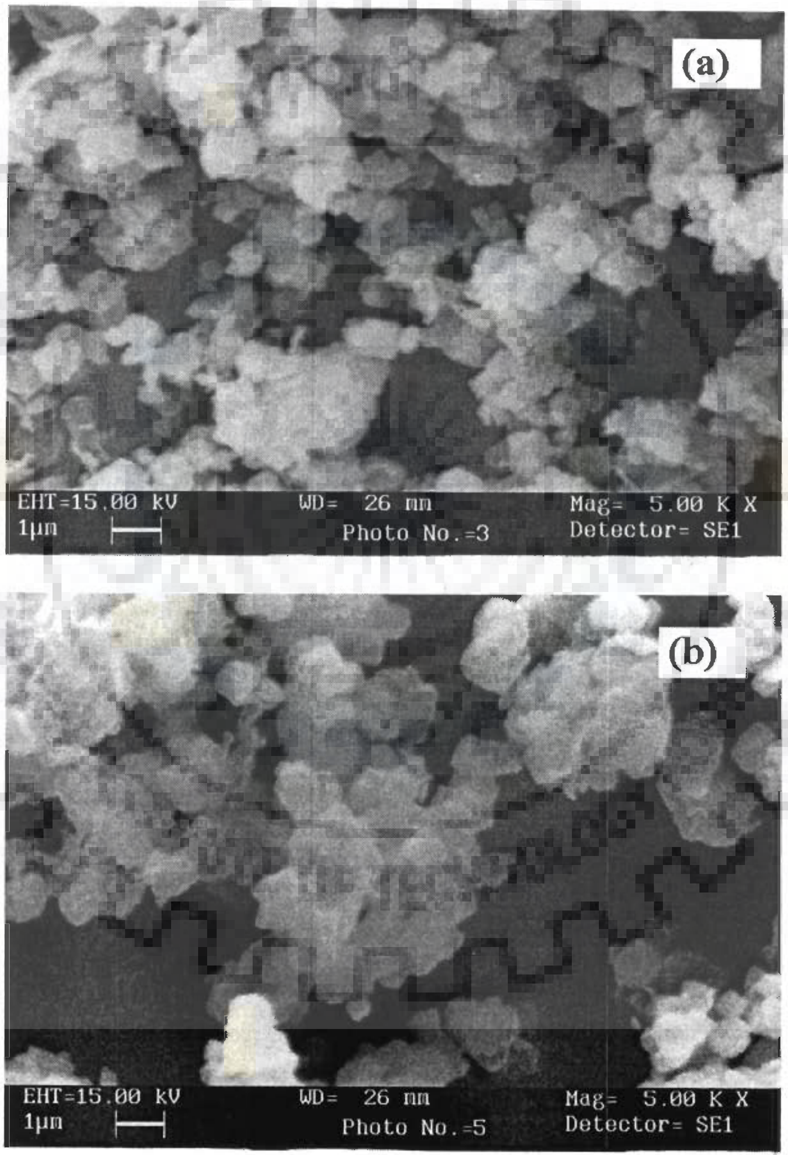


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Figure 2.2. Scanning electron micrograph of (a) OV(IV)-Y and (b) [VO_2(sal-ambmz)]-Y.

2.3.4. Thermogravimetric analysis

The thermal decomposition of catalysts [VO_2(sal-ambmz)]-Y (**2.1**) and [Cu(sal-ambmz)Cl]-Y (**2.2**) usually occurs in two major steps. An endothermic weight loss of ca. 4 % (in **2.1**) or ca. 7 % (in **2.2**) occurs in the temperature range 150 to 250 °C which is possibly due to the removal of intrazeolite water. The second step of exothermic weight loss consists of several sub steps and starts immediately after first step and continue till 800 °C to constant weight. A weight loss of ca. 7 % (in **2.1**) or ca. 10 % (in **2.2**) due to the slow decomposition of metal complexes is expected in this wide temperature range. The loss in small percentage indicates the insertion of only small amount of metal complexes in the cavity of the zeolite-Y. This is in agreement with the low percentage of metal content obtained for encapsulated complexes.

2.3.5. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na–Y, OV(IV)–Y, Cu(II)–Y, [VO_2(sal-ambmz)]-Y and [Cu(sal-ambmz)(Cl)]-Y were recorded at 2θ values between 5 and 70 to see their crystalline nature and to ensure encapsulation of complexes inside the cavity. The XRD patterns of Na–Y, Cu(II)–Y and encapsulated complex [Cu(sal-ambmz)Cl]-Y are presented in Figure 2.3. An essentially similar pattern in Na–Y, metal exchanged zeolite-Y and metal complex encapsulated zeolite-Y was noticed, though slight change in the intensity of the bands in later two cases were in order. These observations indicate that the framework of the zeolite has not undergone any significant structural change during incorporation of the catalysts. This is further, in consultation with SEM, suggests that the crystallinity of the zeolite-Y is preserved during encapsulation. No new peaks could be detected in metal exchanged or complex encapsulated zeolite samples probably due to poor loading of these in zeolite framework.

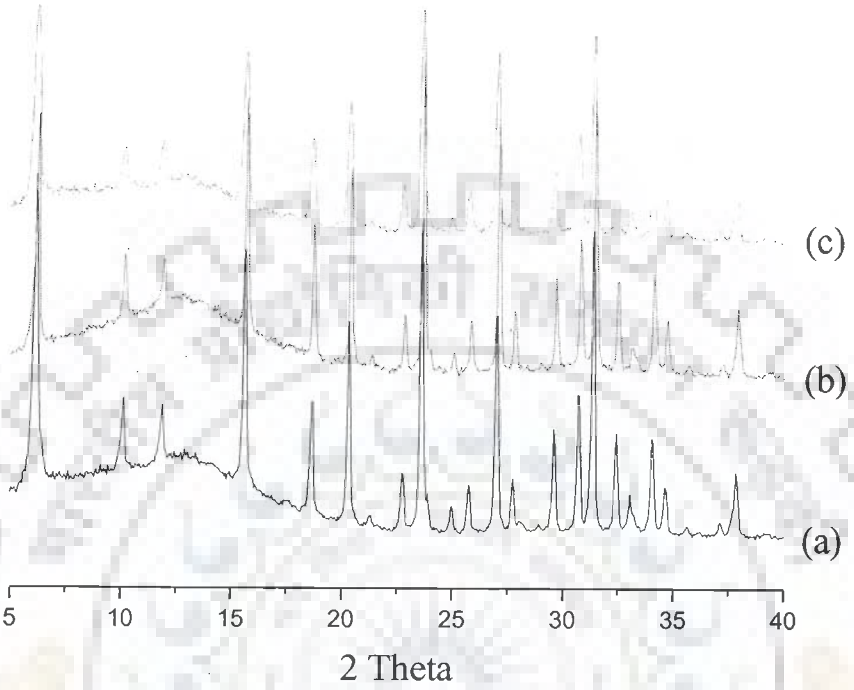


Figure 2.3. XRD pattern of Na-Y (a), Cu-Y (b) and [Cu(sal-ambmz)Cl]-Y (c).

2.3.6. IR spectral studies

A partial list of IR spectral data is presented in Table 2.2. IR spectrum of ligand exhibits two sharp bands at 1617 and 1634 cm^{-1} due to υ(C=N) (azomethine / ring) stretch. These bands move towards lower wave numbers on coordination of azomethine / ring nitrogen to the metal. The presence of hydrogen bonding between NH of benzimidazile and other electronegative atoms in ligand is indicated by the appearance of several medium intensity band in the range 2500 – 2700 cm^{-1}. These bands are also present in complexes indicating the presence of hydrogen bonding in complexes. The coordination of the phenolic oxygen could not be ascertained unequivocally due to the appearance of strong band in the ca. 3400 cm^{-1}. However, in the light of structurally characterized complex e.g. [VO_2(sal-aebmz)](Hsal-aebmz = Schiff base derived from salicylaldehyde and 2-aminoethylbenzimidazole), a monobasic tridentate ONN behaviour of the ligand may also be considered here [144]. Location of bands due to *cis*-VO_2 structure in zeolite encapsulated vanadium complex has not been possible due to appearance of a strong and broad band at ca. 1000 cm^{-1} due to zeolite frame work; neat complex [VO_2(sal-ambmz)] exhibits two bands at 940 and 908 cm^{-1}.

2.3.7. Electronic spectral studies

Table 2.2 also presents electronic spectral data of ligand and complexes. The electronic spectral studies of ligand Hsal-ambmz and its dioxovanadium(V) complex [VO_2(sal-ambmz)] have been discussed in detail [144]. Similar spectral patterns were observed with neat as well as encapsulated vanadium complexes; Figure 2.4a. Encapsulated as well as neat copper complexes also exhibit similar spectral patterns in the UV region. Additional band at ca. 645 nm was observed in neat [Cu(sal-ambmz)Cl] due to d – d transition; Figure 2.4b.

Table 2.2. IR and electronic spectral data of ligand, pure and encapsulated complexes

Compound	IR (cm^{-1})	λ_{max} (nm)
	υ(C=N)(azomethine/ring)	
Hsal-ambmz	1636, 1617	207, 256, 274, 281, 324
[VO_2(sal-ambmz)]-Y	1625, 1600	207, 267, 314, 395
[Cu(sal-ambmz)Cl]-Y	1633, 1536	204, 276, 367
[VO_2(sal-ambmz)]	1624, 1599	218, 257, 274, 281, 320, 384
[Cu(sal-ambmz)Cl]	1634, , 1600	221, 240, 272, 278, 374, 645

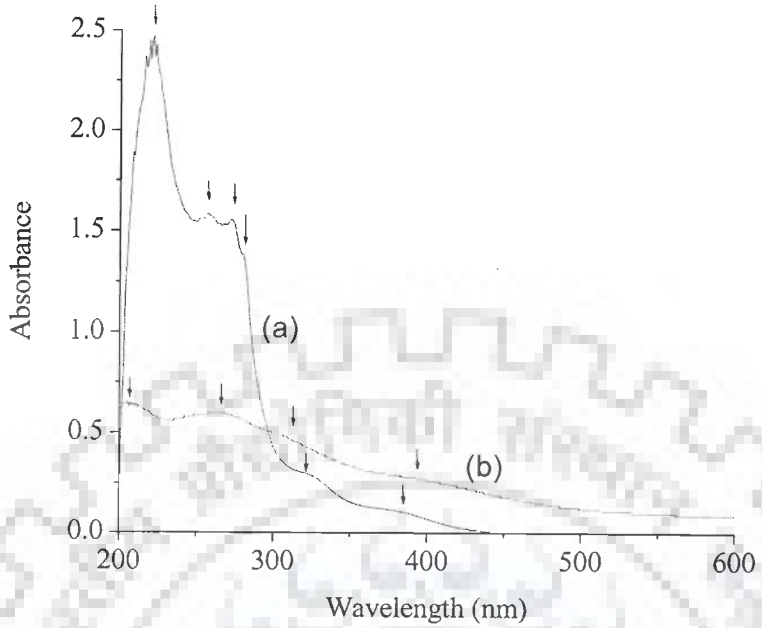


Figure 2.4a. Electronic spectra of [VO$_2$(sal-ambmz)] (a) and [VO$_2$(sal-ambmz)]-Y (b).

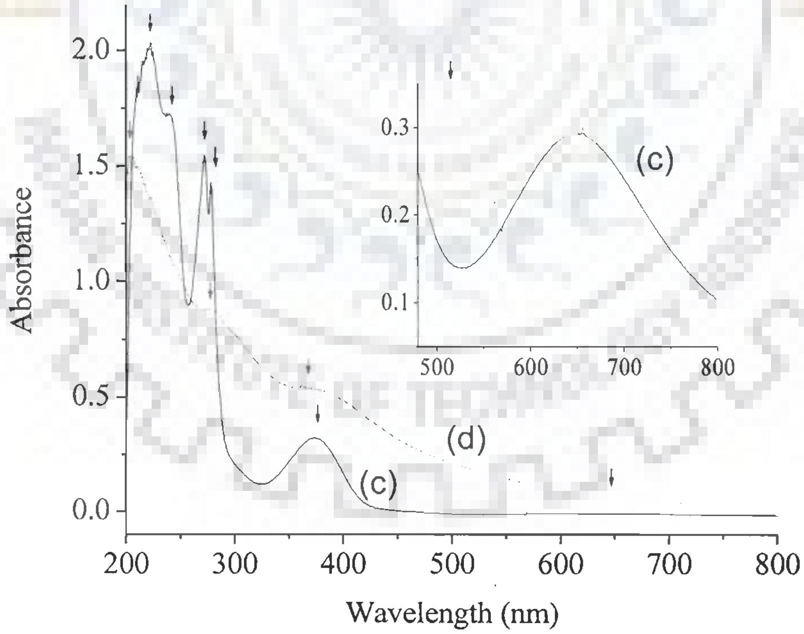
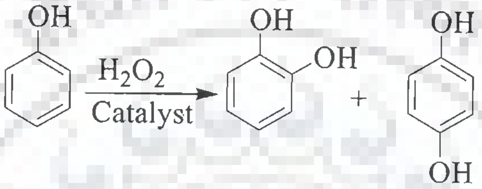


Figure 2.4b. Electronic spectra of [Cu(sal-ambmz)Cl] (c) and [Cu(sal-ambmz)Cl]-Y(d).

2.3.8 Catalytic activity studies

2.3.8.1. Oxidation of phenol

Oxidation of phenol, catalysed by [VO_2(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y was carried out using H_2O_2 as an oxidant and as expected, based on directing group of phenol, two major products i.e. catechol and hydroquinone as shown by Scheme 2.2 were identified from the reaction mixture.



Scheme 2.2

In order to achieve suitable reaction conditions for the maximum oxidation of phenol, the effect of following reaction parameters were studied in detail using [VO_2(sal-ambmz]-Y as a representative catalyst:

- H_2O_2 concentration (moles of H_2O_2 per mole of phenol)
- Amount of catalyst per mole of phenol
- Temperature

The results of all these studies and possible explanations are summarised below.

The effect of H_2O_2 concentration on the oxidation of phenol is illustrated in Figure 2.5. Four different H_2O_2/ phenol molar ratios viz. 1:1, 2:1, 3:1 and 4:1 were considered while keeping the fixed amounts of phenol (4.7 g, 0.05 mol) and catalyst (0.025 g) in 2 ml of MeCN and the reaction was carried out at 75 °C. It is clear from the plot presented as a function of time that the 3:1 molar ratio is best ratio to obtain the phenol conversion of 42.5 % at 75 ° C while 2:1 and 1:1 gave lower conversions. About 6 h was required to establish the equilibrium. Though, H_2O_2 / phenol molar ratio of 4:1 gives relatively higher conversion, the selectivity of H_2O_2 would go considerably low. Induction period of ca. 1 h in each plot suggests that either formation of the reactive intermediate takes longer time itself or intermediate formed takes longer time to transfer oxygen to the substrate.

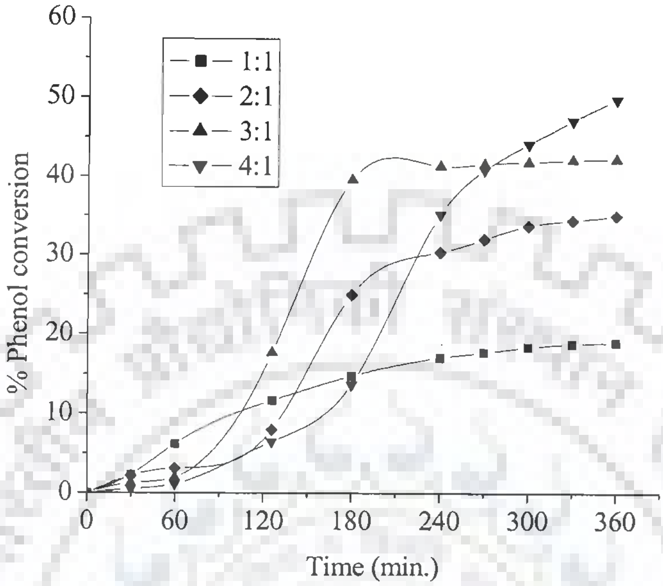


Figure 2.5. Effect of H_2O_2 concentration (H_2O_2 : Phenol) on phenol oxidation.

Similarly, for phenol (4.7 g, 0.05 mol), H_2O_2 (17.01 g, 0.15 mol) and acetonitrile (2 ml), four different amount of catalyst viz.0.015, 0.025, 0.050 and 0.075 g were considered and the reactions were monitored at 75 °C. Results illustrated in Figure 2.6 for the oxidation of phenol shows that 0.015 g catalyst gives only 38.6 % conversion, while 0.025 g catalyst is sufficient enough to obtain 42.5 % phenol conversion at 75° C in 6 h of reaction time. Further increments of catalyst hardly improve the conversion. This has been interpreted in terms of the thermodynamic and mass transfer limitations at higher reaction rates.

The temperature of the reaction medium also influences the reaction rate. It has been inferred that 80 °C is the best suited temperature for the maximum oxidation of phenol. At this temperature, a maximum of 43.9 % conversion was achieved in 6 h of contact time when phenol (4.7g, 0.05 mol), H_2O_2 (17.01 g, 0.15 mol) and [VO(sal-ambmz)] (0.025 g) were taken in 2 ml of acetonitrile. As shown in Figure 2.7, running the reaction at lower temperature viz. 70 °C and 75 °C lower the conversion.

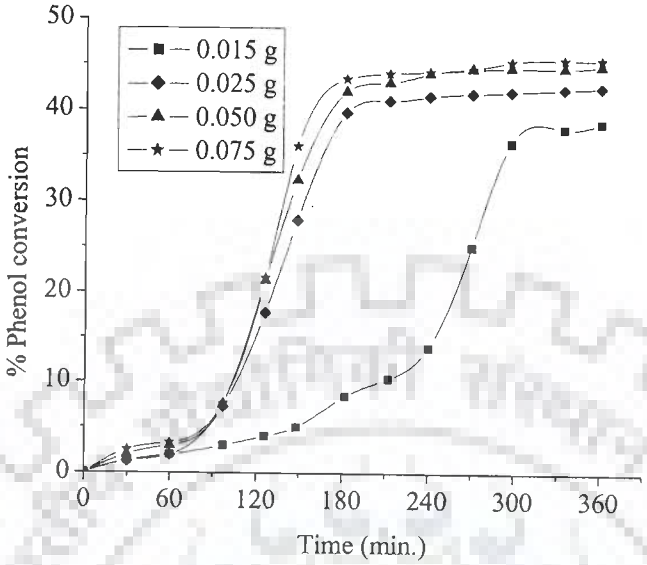


Figure 2.6. Effect of amount of catalyst per unit weight of phenol.

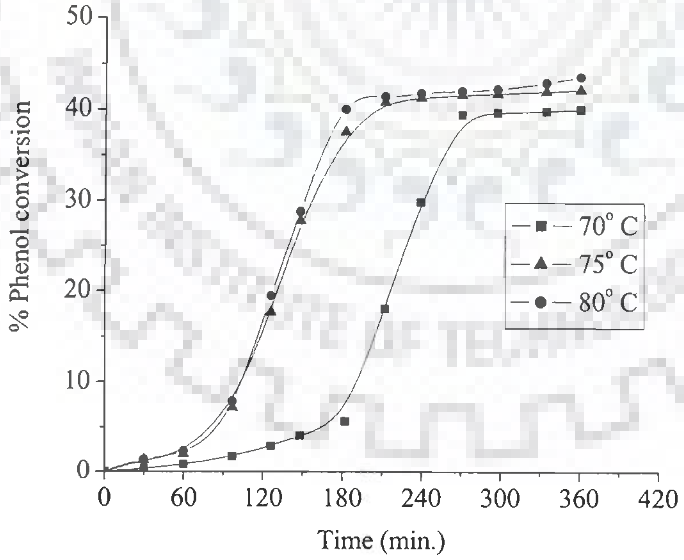


Figure 2.7. Effect of temperature on the oxidation of phenol.

Thus, optimized operating reaction conditions for the maximum oxidation of phenol were fixed as follows: phenol (4.7 g, 0.05 mol), H_2O_2 (17.01 g, 0.15 mol), catalyst (0.025 g), CH_3CN (2 ml) and temperature (80 °C). Under this condition, the performances of other catalysts were studied and the percentages of phenol oxidation after 6 h of reaction time along with the products selectivity are presented in Table 2.3 and the conversion plotted as a function of time is presented in Figure 2.8. With 42.0 % conversion of phenol, [Cu(sal-ambmz)Cl]-Y exhibits nearly identical potentiality to that of [VO_2(sal-ambmz)]-Y. However, the order of the percent conversion is: [VO_2(sal-ambmz)]-Y (43.9 %) > [Cu(sal-ambmz)Cl]-Y (42.0 %). Amongst the products formed, the selectivity of catechol is better and varies between 65.2 to 73.9 %, while that of hydroquinone between 26.1 – 34.8 %. The performances of neat complexes [VO_2(sal-ambmz)] and [Cu(sal-ambmz)Cl] under the above reaction conditions are also good and the conversions follow the order: [VO_2(sal-ambmz)] (37.6 %) > [Cu(sal-ambmz)Cl] (35.4 %). However, the overall performance of encapsulated complexes is better than the corresponding neat ones. The turns over frequencies (TOF) of the encapsulated complexes are also higher.

Table 2.3. Percentage conversion of phenol along with TOF values and the selectivity of the products formed after 6 h of reaction time

Catalyst	% conversion	TOF[a] (h^{-1})	% selectivity	
			Catechol	Hydroquinone
[VO_2(sal-ambmz)]-Y	43.9	194.9	65.2	34.8
[Cu(sal-ambmz)Cl]-Y	42.0	565.7	73.9	26.1
[VO_2(sal-ambmz)]	37.6	167.1	71.4	28.6
[Cu(sal-ambmz)Cl]	35.4	477.9	68.8	31.2

[a]TOF h^{-1} (Turn over frequency) moles of substrate converted per mole of metal (in the solid state catalyst) per hour

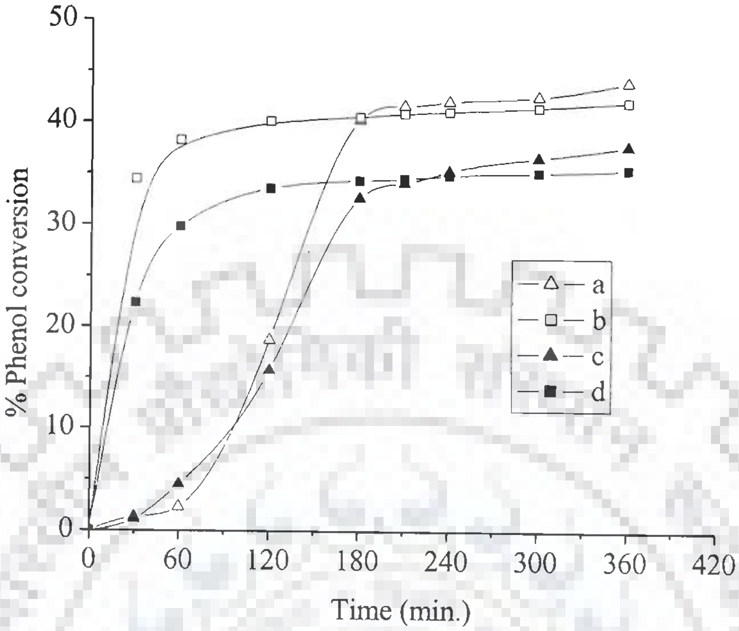
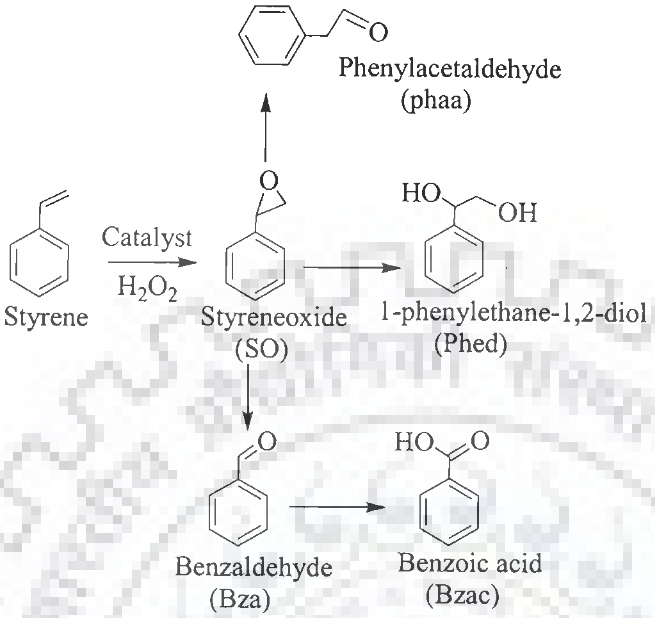


Figure 2.8. Effect of catalysts [VO_2(sal-ambmz)]-Y(a), [Cu(sal-ambmz)Cl]-Y(b), [VO_2(sal-ambmz)]-Y (c) and [Cu(sal-ambmz)Cl] (d) on the oxidation of phenol.

The catalytic performances of these encapsulated complexes compare well with the data reported in the literature. For example, the observed conversions for zeolite-Y encapsulated complexes [Cu(salpn)]-Y (H_2salpn = N,N′-bis(salicylidene)propane-1,3-diamine) (31 %) [37], Cu(saldien)]-Y (46 %) [67], [VO(salen)]-Y (32.6 %) [59] are close to the one reported in Table 2.3. Catalyst NH_4[VO(sal-inh)]-Y (H_2sal-inh = Schiff base derived from salicylaldehyde and iso nicotinic acid hydrazide) exhibits only 26.5 % conversion [82]. However, selectivity towards the formation of catechol for complexes reported here is less (65.2 - 73.9 %) than the reported value of ca. 90 %.

2.3.8.2. Oxidation of styrene

[VO_2(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y also catalyse the oxidation of styrene in presence of H_2O_2 and give styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde along with only minor amounts of unidentified products. Scheme 2.3 represents the formation of all these products. These identified products are common and are observed by others as well [140-144].



Scheme 2.3

In order to achieve suitable reaction conditions for a maximum oxidative conversion of styrene, [VO_2(sal-ambmz)]-Y was taken as a representative catalyst and three different parameters, viz. amount of oxidant and catalyst were varied. The effect of H_2O_2 concentration on the oxidation of styrene is illustrated in Figure 2.9. At a styrene to 30 % H_2O_2 molar ratio of 1:1, a maximum of 53.1 % conversion was achieved in 6 h of contact time for styrene (5 mmol), [VO_2(sal-ambmz)]-Y (0.015 g), 30 % H_2O_2 (0.57 g, 0.005 mol), acetonitrile (10 ml) and temperature (75 °C). Increasing the ratio to 1:2 improved the conversion to 82.3 %, while 1:3 ratio has shown a maximum of 98.2 % conversion. Further increment of H_2O_2 shows no improvement in conversion.

Similarly for three different amounts (viz. 0.005, 0.015, and 0.025 g) of catalyst and H_2O_2 to styrene molar ratio of 3:1 under above reaction conditions, 0.005 g gave only 29.5 % oxidative conversion while 0.015 and 0.025 g have shown nearly identical results with ca. 97 % conversion in 6 h of contact time; Figure 2.10. Thus, 0.015 g catalyst may thus be considered sufficient enough to run the reaction under above conditions.

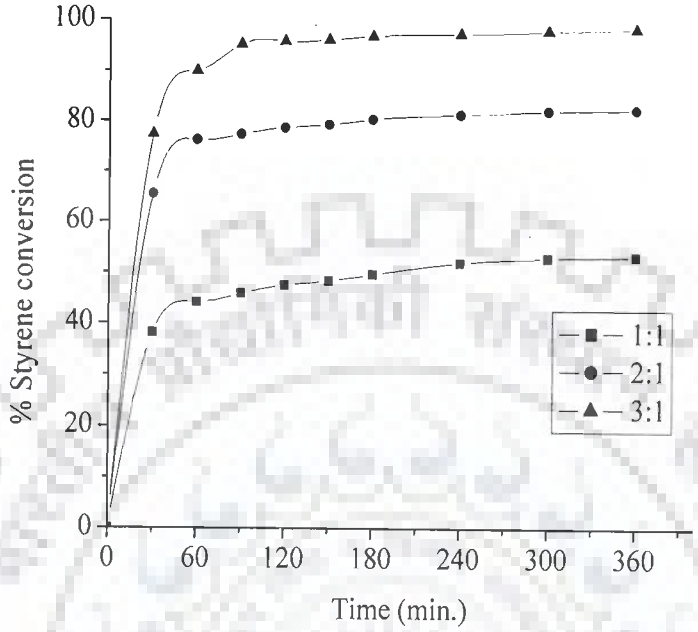


Figure 2.9. Effect of H_2O_2 concentration (H_2O_2 : styrene molar ratio) on oxidation of styrene.

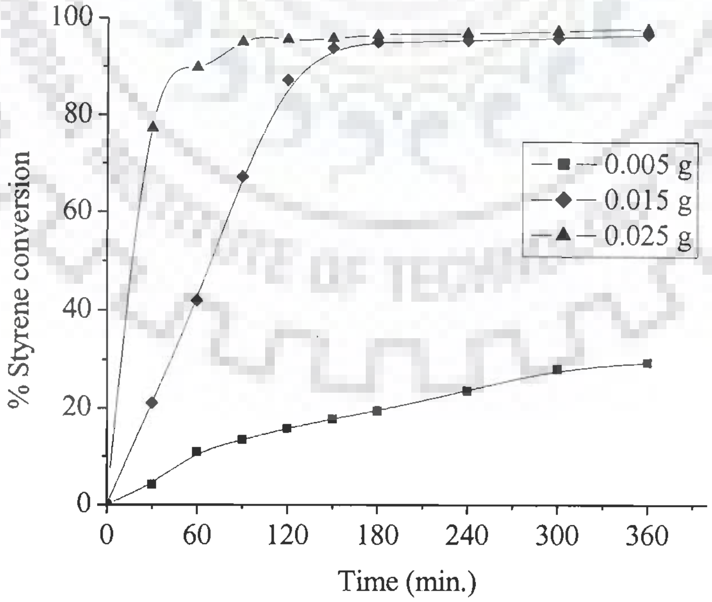
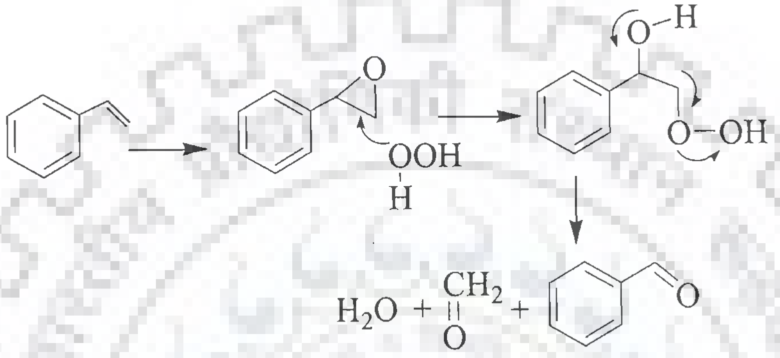


Figure 2.10. Effect of amount of catalyst per unit weight of styrene.

After acquiring the optimized reaction conditions for [VO$_2$(sal-ambmz)]-Y, catalyst [Cu(sal-ambmz)Cl]-Y was also tested under the same reaction conditions. Thus, for 5 mmol of styrene, 15 mmol of 30 % H_2O_2 and 0.015 g of [Cu(sal-ambmz)Cl]-Y were taken in 10 ml of CH_3CN and the reaction was carried out at 75 ° C. Analysis after 6 h of reaction time showed 63.4 % conversion which is less than that observed for [VO$_2$(sal-ambmz)]-Y. Catalytic activity of neat complexes [VO$_2$(sal-ambmz)] and [Cu(sal-ambmz)Cl] have also been carried out. Figure 2.11 provides percentage conversion of styrene as a function of time for various catalysts. A comparative report dealing with the conversion of styrene and selectivity of various products are summarized in Table 2.4. It is clear from the table that neat complex [VO$_2$(sal-ambmz)] exhibits 92.5 % conversion of styrene in 6 h which is equally good to that of respective encapsulated one, while [Cu(sal-ambmz)Cl] registers only 37.2 % conversion which is much less than the respective encapsulated one (56.7 %). The turn over rates calculated for these neat complexes are 68.4 and 83.6, respectively. These values are less than that observed for encapsulated complexes. More over, the recycle ability, easy recovery of the encapsulated catalysts and almost no leaching of complexes during reaction make them better catalysts over the neat ones.

Independent of the type of catalyst, the selectivity of various reaction products follow the order: benzaldehyde >1-phenylethane-1,2-diol > benzoic acid > styrene oxide > phenyl acetaldehyde. The formation of an important component styrene oxide is low in all cases. A highest yield of benzaldehyde is possibly due to further oxidation of styrene oxide formed in the first step by a nucleophilic attack of H_2O_2 on styrene oxide followed by cleavage of the intermediate hydroperoxystyrene, Scheme 2.4 [142]. The formation of benzaldehyde may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via a radical mechanism. High amount of water present in H_2O_2 is partly responsible for the possible hydrolysis of styrene oxide to 1-phenylethane-1,2-diol. Other products e.g. benzoic acid formation through further oxidation of benzaldehyde is not so high in all reactions. Similarly the formation of phenylacetaldehyde through isomerisation of styrene oxide is less in all cases.



Scheme 2.4

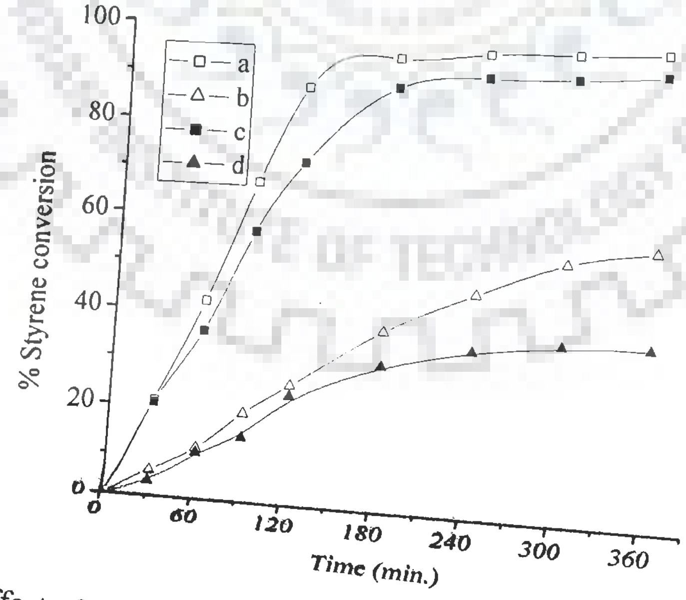


Figure 2.11. Effect of [VO_2(sal-ambmz)]-Y (a), [Cu(sal-ambmz)Cl]-Y (b), [VO_2(sal-ambmz)]-Y (c) and [Cu(sal-ambmz)Cl] (d) on the oxidation of styrene.

Table 2.4. Products selectivity and percent conversion of styrene after 6 hr of reaction time

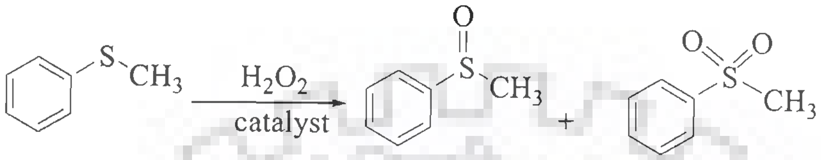
Catalyst	% Conv.	TOF (h^{-1})	% Selectivity[a]					
			so	bza	phed	bzac	phaa	Other
$[VO_2$(sal-ambmz)]-Y	97.0	71.8	5.4	54.9	25.3	13.2	0.2	1.0
[Cu(sal-ambmz)Cl]-Y	56.7	127.4	5.6	51.1	6.3	19.9	13.2	3.5
$[VO_2$(sal-ambmz)]	92.5	68.4	6.8	56.2	23.2	11.6	1.7	0.5
[Cu(sal-ambmz)Cl]	37.2	83.6	4.2	63.1	12.8	11.5	4.6	3.8

[a] so: Styrene oxide, bza: Benzaldehyde, phed: 1-phenylethane-1,2-diol , bzac: Benzoic acid , phaa: Phenyl acetaldehyde

Catalytic potential of these complexes can not be compared directly with similar complexes due to limited literature. Zeolite-Y encapsulated catalyst [Mn(salen)]-Y exhibits ca. 30 % conversion of styrene using molecular oxygen as an oxidant in excess of *tert*-butylhydroperoxide as initiator [153]. About 80 % conversion of styrene was noted with polymer supported catalyst PS-K$[VO_2$(sal-ohyba)] (H_2sal-ohyba = Schiff base derived from salicylaldehyde and *o*-hydrobenzylamine). The selectivity of styrene oxide in all these catalysts is always low [6].

2.3.8.3. Oxidation of methyl phenyl sulfide (thioanisol)

The sulfur atom of the methyl phenyl sulfide is electron rich and has been shown to undergo electrophilic oxidation to give sulfoxide. Such oxidation of methyl phenyl sulfide was tested using $[VO_2$(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y as catalyst. Using the fixed amount of methyl phenyl sulfide (0.62 g, 0.005 mol), catalyst $[VO_2$(sal-ambmz)]-Y (0.015 g) and H_2O_2 (0.285 g, 0.0025 mol) in 20 ml of CH_3CN and running the reaction at room temperature gave 47.1 % conversion with a mixture of two products, methyl phenyl sulfoxide and methyl phenyl sulfone, Scheme 2.5. Increasing the oxidant amount to 0.005 mol i.e. at 1:1 substrate to oxidant molar ratio, this conversion reached to 97.3 % within 2 h of contact time. The results obtained and reaction conditions used suggested using substrate to oxidant ratio of 1:1 to obtain the maximum oxidation of methyl phenyl sulfide oxidation.



Scheme 2.5

In order to optimize the amount of catalyst under above operating conditions, four different amounts of catalyst (viz. 0.001, 0.005, 0.010 and 0.015 g) were considered and the results obtained are presented in Figure 2.12. It turns out from the figure that 0.005 g of catalyst was sufficient enough to give a maximum of 96.1 % conversion of methyl phenyl sulfide with the percent selectivity for methyl phenyl sulfoxide of 97.1 and methyl phenyl sulfone of 2.9. Increasing the amount to 0.010 and 0.015 g marginally affect the conversion as well selectivity. Under similar conditions neat complex [VO_2(sal-ambmz)] gave a maximum conversion of 91 % where selectivity of major product was 98 %. Thus, neat as well as encapsulated complexes both are highly selective towards sulfoxide formation. A blank reaction under similar conditions i.e. methyl phenyl sulfide (0.005 mol), H_2O_2 (0.005 mmol) and CH_3CN (20 ml), resulted in 37 % conversion of methyl phenyl sulfide, where 69.3 % selectivity was registered for sulfoxide and 30.7 % for sulfone. Thus, these complexes not only enhance the percent conversion of methyl phenyl sulfide, they also improve the selectivity for sulfoxide. However, encapsulated complex may be considered as better catalyst as recovery of the catalyst becomes easier and its turn over rate is also high in comparison to the neat one. Table 2.5 summarizes products selectivity and conversion details. On the contrary, neat as well encapsulated copper complexes do not affect the conversion of methyl phenyl sulfide and thus they are catalytically inactive for sulfide oxidation.

Table 2.5. Percent conversion of thioanisol and selectivity of sulfoxide and sulfone formation at room temperature after 2 h of contact time

Catalyst (0.005 g)	% Conversion	TOF h^{-1}	% Selectivity	
			sulfoxide	sulfone
[VO_2(sal-ambmz)]-Y	96.1	640.20	97.1	2.9
[VO_2(sal-ambmz)]	91.0	201.32	98.0	2.0
Without catalyst	37.0	-	69.3	30.7

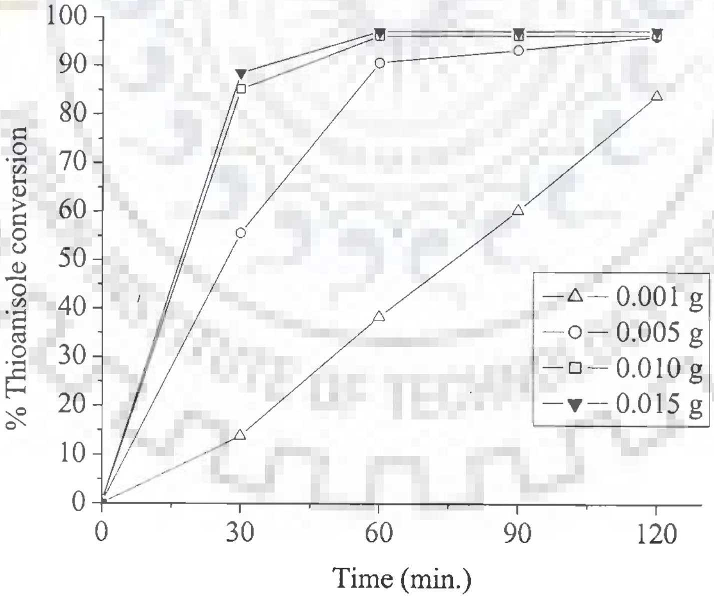


Figure 2.12. Effect of catalyst weight on thioanisol oxidation.

2.3.9. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the neat complexes were treated with H_2O_2 and progress of the reaction was monitored by electronic absorption spectroscopy; Figure 2.13. Thus, the titration of methanolic solution of [VO_2(sal-ambmz)] with one-drop portions of 30 % H_2O_2 dissolved in methanol resulted in the gradual shift of 384 nm band to 380 nm along with the decrease in band maximum while band at 320 nm recorded only increase in intensity. Other two bands appearing at 274 and 281 nm showed very slight increase in intensity. The UV band at 257 nm showed trend of increasing intensity only and finally disappeared. We interpret these changes due to the formation of oxoperoxovanadium(V) complex [$VO(O_2)$(sal-ambmz)]. Such oxoperoxovanadium(V) complexes with e.g. Hsal-aebmz, a closely related ligand, has been prepared and characterized. The final spectral pattern of [VO_2(sal-ambmz)] is also similar to the known complex [$VO(O_2)$(sal-aebmz)] [144]. Thus, the formation of an intermediate oxoperoxovanadium(V) complex may be proposed which finally transfers oxygen to the substrates.

The addition of one-drop portions of 30 % H_2O_2 dissolved in methanol to a methanolic solution of [Cu(sal-ambmz)Cl] resulted in the quick reduction in the intensity of d-d band at 645 nm without changing its position followed by a slow increase in band maximum on further addition of H_2O_2. The band at 374 nm experienced decrease in intensity, while a shoulder appearing at 298 nm slowly disappeared. Other two bands at 278 and 271 nm slowly gained intensity, and the band at 240 nm gained intensity but finally disappeared. Figure 2.14 presents spectral changes observed. All these suggest the interaction of H_2O_2 with Cu(II) centre.

At least three types of intermediates having copper-oxygen interaction viz. side-on Cu^{III}–(μ-η^2–peroxo)–Cu^{III}, bis(μ–oxo–Cu^{III}) and Cu^{III}–O–O–H (copper-hydroperoxide) have been reported in the literature during catalytic action [154, 155]. The facile formation of [(HOO)-Cu(sal-ambmz)Cl] intermediate is expected in zeolite-encapsulated copper complex as only monomeric species is present in the cavity. A quick decrease in the intensity of 645 nm band may be due to interaction of H_2O_2 to [Cu(sal-ambmz)Cl] while increment in intensity of 271 and 278 nm bands may possibly be due to the formation of hydroperoxide [HOO)-Cu(sal-ambmz)Cl] intermediate of the neat complex. Hydroperoxocopper complexes are known to exhibit a charge transfer band at ca. 600 nm [156]. The decrease in intensity of 645 nm band without any isosbestic point in neat complex may possibly be due to the merging of this additional charge transfer band with d-d transition. The intermediate finally transfers coordinated oxygen atoms to the substrates to give the products. Thus, the catalytic performance of encapsulated catalyst could be attributed to the formation of facile and reversible intermediate species.

2.3.10. Test for recycle ability and heterogeneity of the reactions

The recycle ability of both the encapsulated complexes has been tested in all three catalytic reactions. In a typical experiment e.g. for styrene, the reaction mixture after a contact time of 6 h was filtered and after activating the catalyst by washing with acetonitrile and drying at ca. 120 °C, it was subjected to further catalytic reaction under similar conditions. No appreciable loss in catalytic activity suggests that complex is still present in the cavity of the zeolite-Y. The filtrate collected after separating the used catalyst was placed into the reaction flask and the reaction was continued after adding fresh oxidant for another 4 h. The gas chromatographic analysis showed no improvement in conversion and this confirms that the reaction did not proceed upon removal of the solid catalyst. The reaction was, therefore, heterogeneous in nature.

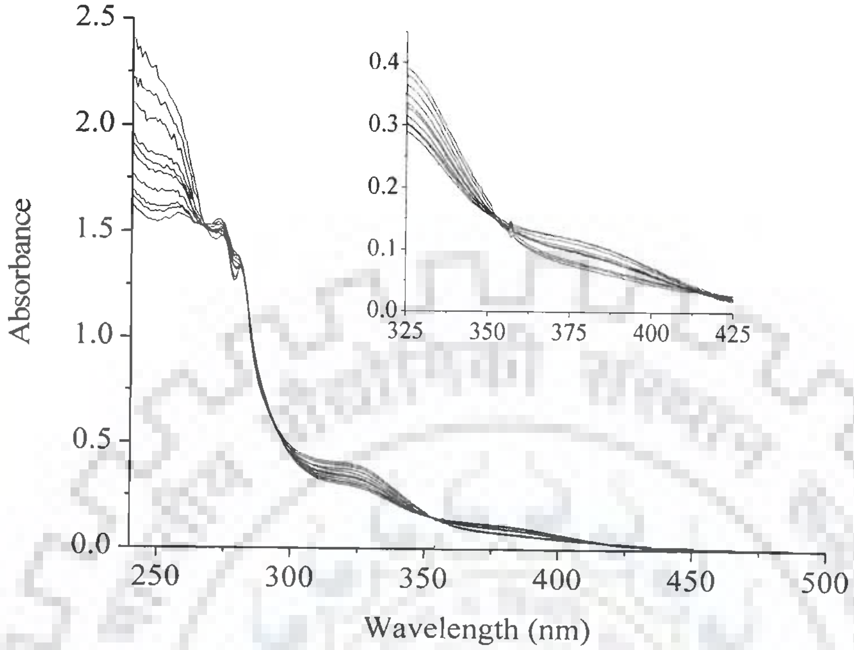


Figure 2.13. Titration of [VO_2(sal-ambmz)] with H_2O_2.

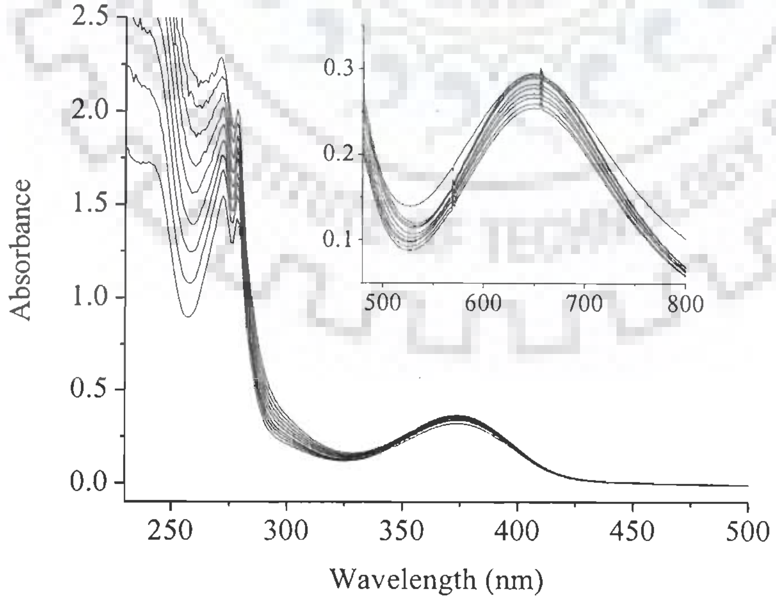


Figure 2.14. Titration of [Cu(sal-ambmz)Cl] with H_2O_2

2.4. CONCLUSIONS

Complexes [VO$_2$(sal-ambmz)] and [Cu(sal-ambmz)Cl] have been encapsulated in the super cages of zeolite-Y. The integrity of encapsulation was confirmed by spectroscopic studies as well as chemical and thermal analysis. These encapsulated complexes are found active for the oxidation of phenol and styrene with good conversion. A maximum of 43.9 % of phenol oxidation was observed with vanadium based catalyst which is followed by copper based catalyst. However, the copper based catalyst is more selective (73.9 %) towards the formation of catechol than the vanadium based catalyst (65.2 %). The oxidation of styrene gives at least four different products, where expected product styrene oxide was found only in small yield (4.2-6.8 %), and the percentage of benzaldehyde was relatively high. Oxidation of methyl phenyl sulfide using zeolite encapsulated vanadium complex has been tested first time, to the best of our knowledge, and as high as 96 % conversion with 97 % selectivity towards methyl phenyl sulfoxide and only 3 % towards methyl phenyl sulfone was observed. It is concluded from the catalytic data and turn over frequency that encapsulated complexes are better catalysts than the neat ones. These catalysts are recyclable without loss of the catalytic potential. They do not leach in any of the catalytic reactions and are heterogeneous in nature.

CHAPTER-3

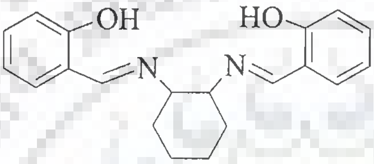
Oxovanadium (IV) and copper(II) complexes of 1, 2-diaminocyclohexane based ligand encapsulated in zeolite-Y for the catalytic oxidation of styrene, cyclohexene and cyclohexane

3.1. INTRODUCTION

Modern catalytic sciences have played an important role in the development of heterogeneous catalysts for new chemical technologies. Amongst heterogeneous catalysts, zeolite encapsulated metal complexes (ZEMC) hold a key place as they have also been suggested as model compounds for enzyme mimicking [15]. This is because zeolites may replace the protein mantle of the enzyme in the model compound. A molecule encapsulated in the zeolite cages is characterized by steric restriction and if the size of the molecule is comparable to the zeolite cage, the molecule in the cage may show interesting properties, which are not encountered under ordinary conditions. All these advantages prompted several research groups to investigate the catalytic properties of the complexes entrapped within the super cages of zeolite-Y [21, 35, 59, 64, 89, 130-132, 139, 143, 157, 158, 190].

The oxyfunctionalization of inexpensive hydrocarbons to produce more valuable organic compounds such as alcohols, aldehydes, and ketones, requires the selective oxidation of strong C–H bonds. Alcohols and ketones are important intermediate materials for the manufacture of many important products, such as, fiber, drugs and fragrance. Chun Jin et al. have encapsulated transition metal tetrahydro-Schiff base complexes in the zeolite-Y and studied their catalytic potentialities for the oxidation of cycloalkanes [159]. Complex [Cu(salen)] catalyses , by peroxide, the oxidation of cyclohexane in moderate yield [160]. Zeolite-Y encapsulated manganese(II) complexes have been used for the oxidation of cyclohexene by *tert*-butylhydroperoxide [75]. Transition metal complexes catalysed oxidation of styrene into a variety of products such as epoxides, carbonyl compounds, diols and oxidative cleavage products of C-C and have received much attention primarily due to interest in selective and partial oxidations [6, 128, 142, 144, 153].

In this paper, we report herein the encapsulation of oxovanadium(IV) and copper(II) complexes of 1,2-diaminocyclohexane based ligand H_2sal-dach (**3.I**, Scheme **3.1**) in the cavity of zeolite-Y by the flexible ligand method. These zeolite encapsulated complexes have, subsequently, been screened as prospective catalysts for the oxidation of styrene, cyclohexene and cyclohexane.



H_2sal-dach (**3.I**)

Scheme 3.1

3.2. EXPERIMENTAL

3.2.1. Materials and methods

Analytical reagents grade cyclohexane and 30% aqueous H_2O_2 were obtained from Ranbaxy, India. Cupric nitrate, cupric chloride, salicylaldehyde, 1,2-diaminocyclohexane were obtained from E. Merck, India. Vanadyl sulfate penta hydrate from Loba Chemie, India and styrene from Acros Organics, New Jersey, U.S.A. were used as such. Y-zeolite (Si/Al ~ 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were of AR grade. [VO(acac)$_2$] was prepared following literature procedure [161]. Instrumental details are given in Chapter 2.

3.2.2. Preparations

3.2.2.1. Preparation of H_2sal-dach

A solution of 1,2-diaminocyclohexane (1.44 g, 10 mmol) in 10 ml methanol was added drop wise to a methanolic solution of salicylaldehyde (2.56 g, 10 mmol in

20 ml) and the reaction mixture was heated under reflux on a water bath for 2 h. After cooling to room temperature, the yellow precipitate of H_2sal-dach was filtered off, washed with hot methanol and dried in vacuo over silica gel. Yield: 80 %. Anal. found C, 74.04 %; H, 6.97 %; N, 8.51 %. Calcd. for $C_{20}H_{22}N_2O_2$ (322): C, 74.53 %; H, 6.83 %; N, 8.70 %. ^{1}H NMR (δ in ppm): 13.68, 13.34 (2:1, s, 2H, OH), 8.58, 8.49 (2:1, s, 2H, -CH=N-), 7.44(d), 7.31-7.32(m), and 6.81-6.90(m) (8H, aromatic), 3.68 (d, 2H, -CH- of cyclohexyl), 1.76-1.87 and 1.56 -1.57 (complex m, 8H, -CH_2- of cyclohexyl).

3.2.2.2. Preparation of M-Y

An amount of 5.0 g of Na-Y zeolite was suspended in 300 ml of distilled water and to this was added 12 mmol of cupric nitrate (for Cu(II)-Y) or vanadyl sulfate (for OV(IV)-Y) with stirring at ca. 90 °C for 24 h. The solid was filtered off and washed with hot distilled water until filtrate was free from any metal ion content, and dried at ca 120 °C for 24 h.

3.2.2.3. Preparation of [Cu^{II}(sal-dach)]-Y (3.1) and [VO^{IV}(sal-dach)]-Y (3.2): A general method

Both encapsulated complexes were prepared using a flexible ligand method, therefore, a general method is outlined here. An amount of 1.0 g of Cu-Y or OV-Y and 2.5 g ligand were mixed in 60 ml of methanol in a round bottom flask and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was filtered and extracted with methanol using Soxhlet extractor to remove excess ligand that remained uncomplexed in the cavities of the zeolite as well as located on the surface of the zeolite along with neat complexes, if any. The remaining uncomplexed metal ions in zeolite were removed by stirring with aqueous 0.01M NaCl solution (200 ml) for 8 h. It was then washed with double distilled water till no precipitate of AgCl was observed in the filtrate on treating with $AgNO_3$.

3.2.2.4. Preparation of [VO^{IV}(sal-dach)]

The ligand H$_2$sal-dach (1.61 g, 5 mmol) dissolved in 20 ml of methanol was added to a solution of [VO(acac)$_2$] (1.33 g, 5 mmol) dissolved in 10 ml of methanol and the reaction mixture was refluxed for 2 h. During this period green solid of [VO(sal-dach)] slowly separated out. After cooling the mixture, it was filtered off, washed with methanol and dried in vacuo over silica gel. Yield: 65 %. Anal. found C, 62.23 %; H, 5.42 %; N, 7.18 %. Calcd. for $C_{20}H_{20}N_2O_3V$ (381): C, 62.99 %; H, 5.25 %; N, 7.35 %.

3.2.2.5. Preparation of [Cu^{II}(sal-dach)]

A solution of Cu(CH$_3$COO)$_2$ .H$_2$O (1.0 g, 5 mmol) dissolved in 20 ml of methanol was added to a hot solution of H$_2$sal-dach(1.61 g, 5 mmol) in 20 ml of methanol, and the reaction mixture was refluxed on a water bath for 2 h. Violet solid of [Cu(sal-dach)] slowly separated out within a few hours period on cooling the solution at ambient temperature. This was filtered off, washed with methanol and dried in vacuo over silica gel. Yield 68 %. Anal. found C, 62.28 %; H, 5.13 %; N, 7.41 %. Calcd. for $C_{20}H_{20}N_2O_2Cu$ (383.54): C, 62.57 %; H, 5.21 %; N, 7.30 %.

3.2.3. Catalytic activity studies

3.2.3.1. Oxidation of styrene

The catalytic oxidation of styrene was carried out using complexes, [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y in a 50 ml flask fitted with a water circulated condenser. In a typical reaction, an aqueous solution of 30 % H_2O_2 (2.28 g, 20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH_3CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The reaction was considered to begin after addition of 0.025 g of catalyst. During the reaction, the products were analyzed using a gas chromatograph by withdrawing small aliquots after specific interval of time and confirming their identity by GC-MS.

3.2.3.2. Oxidation of cyclohexene

The catalytic oxidation of cyclohexene was also carried out using both the catalysts. In a typical reaction, an aqueous solution of 30 % H_2O_2 (2.28 g, 20 mmol), cyclohexene (0.82 g, 10 mmol) and catalyst (0.035 g) were mixed in 20 ml of CH_3CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The progress of the reaction was monitored as mentioned above and identity of the various products confirmed by GC-MS.

3.2.3.3. Oxidation of cyclohexane

Aqueous solution of 30 % H_2O_2 (2.28 g, 20 mmol), cyclohexane (0.84 g, 10 mmol) and catalyst (0.035 g) were mixed in 5 ml of CH_3CN and the reaction mixture was heated at 70 °C with continuous stirring in an oil bath for 2 h. The formation of the reaction products and their identity were confirmed as mentioned above.

3.3. RESULTS AND DISCUSSION

3.3.1. Characterization of catalysts

Synthesis of complexes [VO(sal-dach)] and [Cu(sal-dach)] encapsulated in the nano-cavity of zeolite-Y involved the exchange of oxovanadium(IV) and copper(II) ions with Na(I) of Na-Y followed by reaction of metal exchanged zeolite-Y with H_2sal-dach in solution. Here, ligand entered into the cavity of zeolite-Y due to its flexible nature and interacted with metal ions. The formation of ligand was confirmed by elemental analysis and ^{1}H NMR spectroscopy (c.f. experimental section)). The percentages of metal content determined before and after encapsulation by inductively coupled plasma along with their expected formula and color are presented in Table 3.1. As crude mass was extracted with methanol, the metal ion content found after encapsulation is only due to the presence of metal complexes in the nano-cavity of the zeolite-Y. The molecular formula of the complexes are based on the neat complexes [VO(sal-dach)] and [Cu(sal-dach)] that have also been prepared by reacting the corresponding suitable metal precursor with the ligand and characterised.

Table 3.1. Chemical composition, physical and analytical data

S. No.	Catalyst	Colour	Metal content (wt %)	Langmuir surface area (m^2/gm)
1	OV(IV)-Y	Light green	4.58	439
2	Cu(II)-Y	Yellow	7.60	752
3	[VO(sal-dach)]-Y	Light green	0.84	241
4	[Cu(sal-dach)]-Y	Pale blue-green	2.61	489

Table 3.1 lists the surface area of VO(IV)–Y, Cu(II)–Y and their encapsulated complexes. As expected, encapsulation of transition metal complexes in zeolite-Y led to an apparent reduction in the surface area and pore volume. Thus, a reduction by about 45 % and 35 % in surface area was observed upon inclusion of [VO(sal-dach)]-Y and [Cu(H_2sal-dach)]-Y, respectively. Nevertheless, the decreasing degree depends on the amount of incorporated complexes as well as their molecular size and geometrical conformation inside the zeolitic host.

3.3.2. Scanning electron micrograph studies

The scanning electron micrographs (SEM) of the metal exchanged zeolite and their respective encapsulated complexes indicate the presence of well defined crystals free from any shadow of the metal ions or complexes present on their external surface. The representative micrographs of (a) Cu(II)-Y and (b) [Cu(sal-dach)]-Y are presented in Figure 3.1.

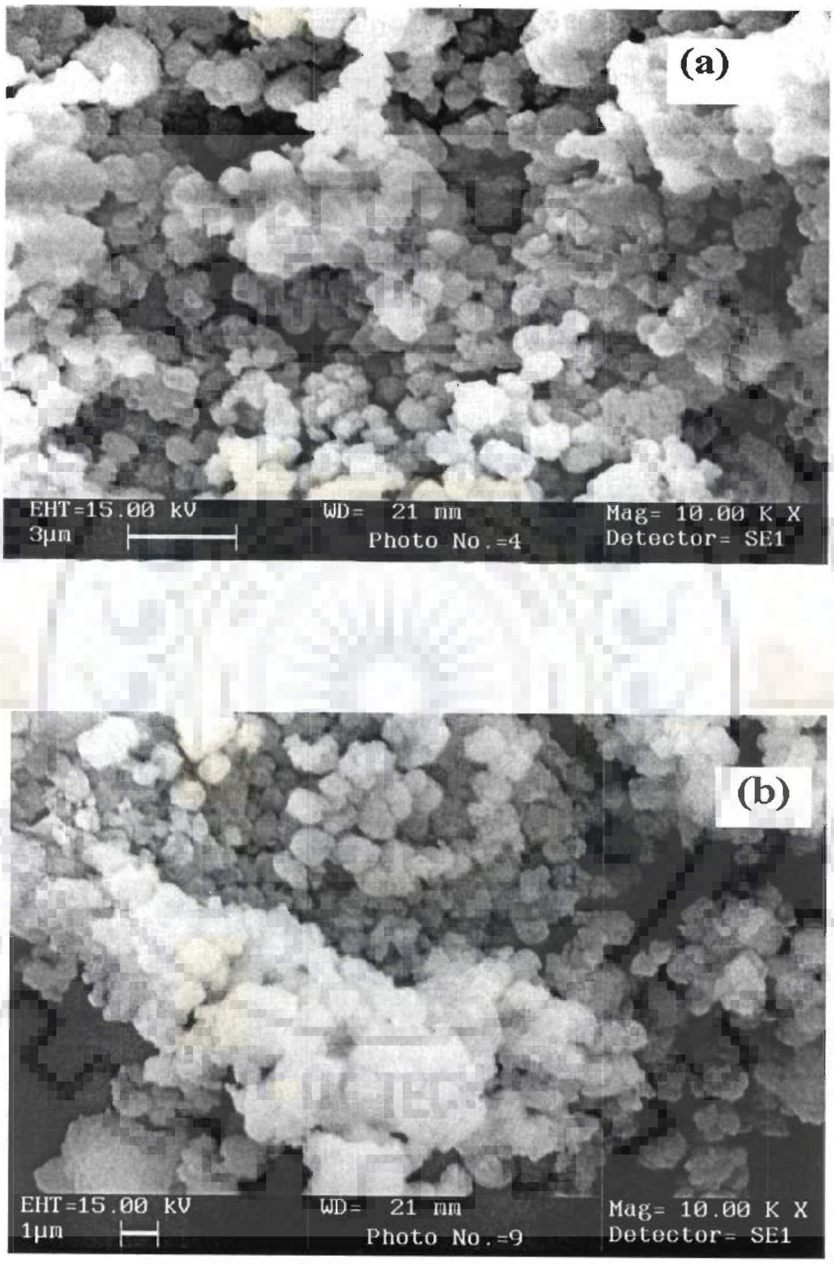


Figure 3.1. Scanning electron micrographs of (a) Cu-Y and (b) [Cu (sal-dach)]-Y.

3.3.3. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na-Y, OV(IV)-Y and Cu(II)-Y and encapsulated metal complexes were recorded at 2θ values between 5 and 70°. The XRD patterns of Na-Y, Cu(II)-Y and zeolite encapsulated complex [Cu(sal-dach)]-Y are presented in Figure 3.2. An essentially similar pattern in Na–Y, metal ions exchanged zeolite and encapsulated metal complexes was noticed, though slight change in the intensity of the bands in encapsulated complexes is in line. These observations indicate that the framework of the zeolite has not undergone any significant structural change during incorporation of the catalysts i.e. crystallinity of the zeolite-Y is preserved during encapsulation. No new peaks due to neat complex were detected in the encapsulated zeolite possibly due to very low percentage loading of metal complexes.

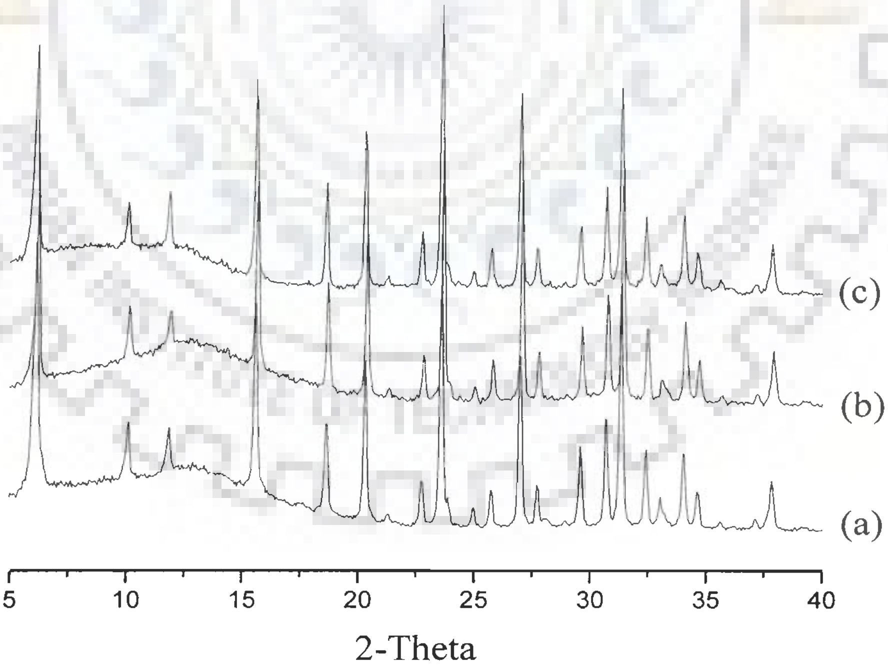


Figure 3.2. XRD pattern of (a) Na-Y, (b) Cu-Y and (c) [Cu(sal-dach)]-Y.

3.3.4. Thermogravimetric analysis

The TG and DTG profile of one representative complex [Cu(sal-dach)]-Y is reproduced in Figure 3.3. Thermograms of catalysts, [VO(sal-dach)]-Y (**3.1**) and [Cu(sal-dach)]-Y (**3.2**) indicate that their decomposition occurs in three steps, though these steps are overlapping. The removal of just trapped water of ca. 6.2 % (in **3.1**) or ca. 5 % (in **3.2**) occurs up to ca.170 °C, while an exothermic weight loss of ca. 7.3 % (in **3.1**) or ca. 6.6 % (in **3.2**) associated with removal of intrazeolite water occurs in the temperature range 170– 350 °C. The third step involves the slow but exothermic weight loss of ca. 7.5 % (in **3.1**) or ca. 7.3 % (in **3.2**) in a wider temperature range (350 – 800 °C) due to decomposition of the chelating ligand. The loss in small percentage indicates the insertion of only small amount of metal complexes in the cavity of the zeolite-Y. This is in agreement with the low percentage of metal content obtained for encapsulated complexes.

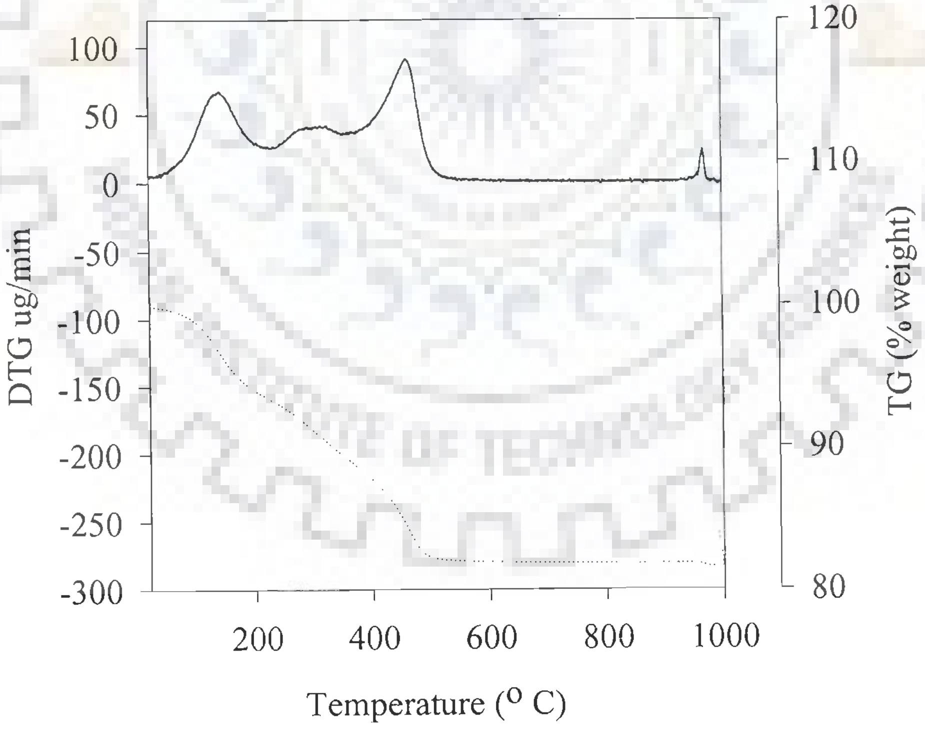


Figure 3.3. TG (dotted line) and DTG (solid line) profile of [Cu(sal-dach))-Y.

3.3.5. IR spectral studies

A partial list of IR spectral data is presented in Table 3.2. The intensity of the peaks in encapsulated complexes is, though, weak due to their low concentration in zeolite matrix, the spectra of encapsulated as well as their neat complexes show essentially similar bands. Comparison of the spectra of these catalysts with the ligand provides evidence for the coordinating mode of ligand in catalysts. The ligand H_2sal-dach exhibits a broad band in the 2450–2750 cm^{-1} due to extensive hydrogen bonding between phenolic hydrogen and nitrogen of azomethine group. Absence of this band in the spectra of encapsulated complexes indicates the destruction of the hydrogen bond followed by the coordination of phenolic oxygen after deprotonation. The sharp band appearing at 1629 cm^{-1} due to ν(C=N) (azomethine), shifts to lower wave number and appears at 1618–1624 cm^{-1}. This indicates the involvement of azomethine nitrogen in coordination. The presence of multiple bonds at 2840-2935 cm^{-1} in ligand and its complexes with slight shift suggests the presence of CH_2 group of cyclohexane in ligand as well as its complexes. Neat complex [VO(sal-dach)] exhibit a sharp band at 990 cm^{-1} due to ν(V=O) stretch, while in zeolite encapsulated vanadium complex location of bands due to ν(V=O) structure has not been possible due to appearance of a strong and broad band at ca. 1000 cm^{-1} due to zeolite frame work.

Table 3.2. IR and electronic spectral data of ligand, pure and encapsulated complexes

Compound	IR (cm^{-1})	λ_{max} (nm)
	ν(C=N)	
H_2sal-dach	1629	207, 226, 268, 337
[VO(sal-dach)]-Y	1621	222, 281, 357
[Cu(sal-dach)]-Y	1624	217,261,346
[VO(sal-dach)]	1618	236, 278, 360, 568
[Cu(sal-dach)]	1622	228, 273, 354, 560

3.3.6. Electronic spectral studies

The electronic spectral data of ligand and complexes are also presented in Table 3.2. The electronic spectral profiles of [VO(sal-dach)] and [VO(sal-dach)]-Y are reproduced in Figure 3.4 while that of [Cu(sal-dach)] and [Cu(sal-dach)]-Y are in Figure 3.5. The electronic spectrum of ligand H_2sal-dach exhibits three bands at 337, 268 and 207 nm and these are assigned due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\phi \rightarrow \phi^*$ transitions, respectively. All these bands shift to higher wave length side indicating the restructuring of the ligand after coordination to the metal ion. Appearance of a week band due to ligand to metal transition underneath of $n \rightarrow \pi^*$ transition make this band broad. While no band could be located in further higher wave length region due to expected d – d transition in the encapsulated complexes; neat complexes exhibit at least one broad band at 568 nm (in [VO(sal-dach)]) or at 560 nm (in [Cu(sal-dach)]).

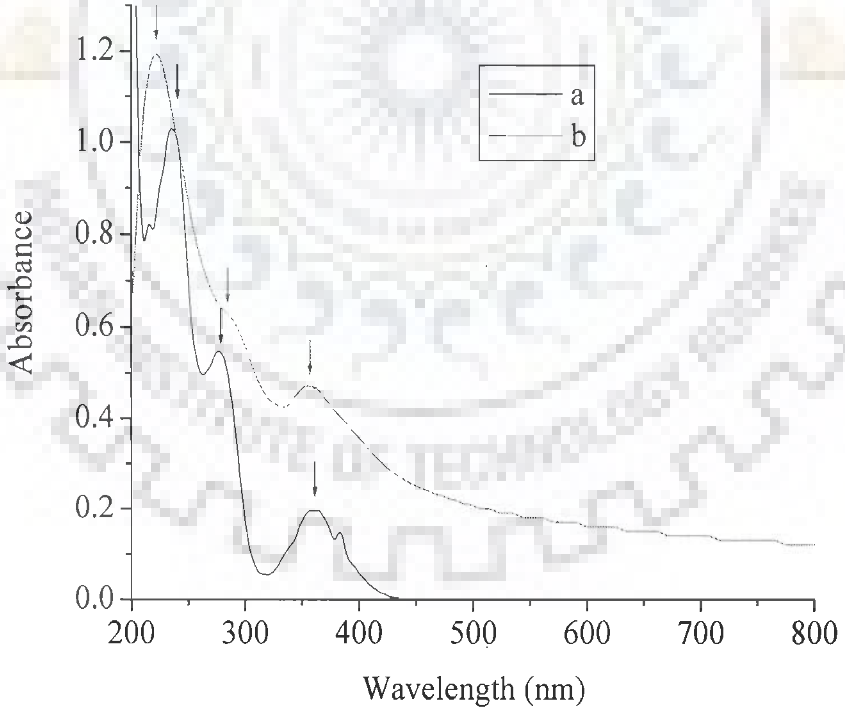


Figure 3.4. Electronic spectra of [VO(sal-dach)] (a) and [VO(sal-dach)]-Y (b).

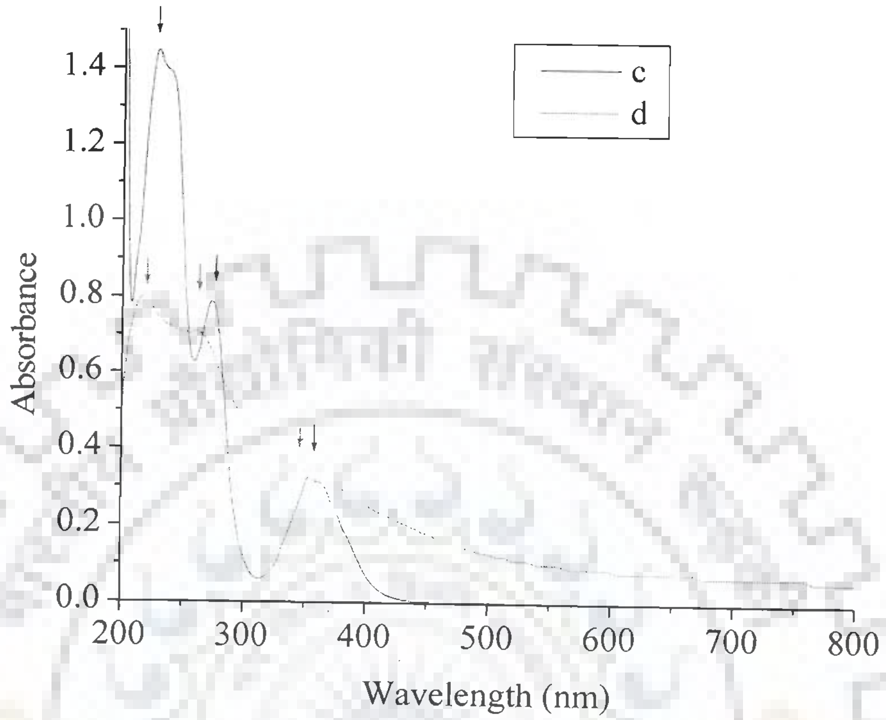
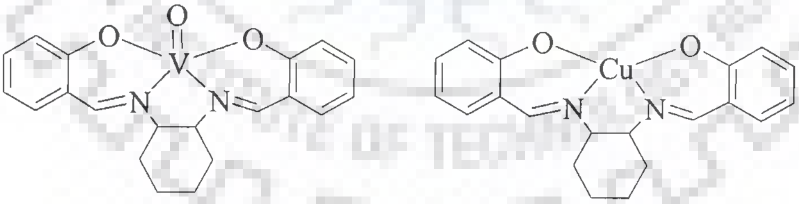


Figure 3.5. Electronic spectra of [Cu(sal-dach)] (c) and [Cu(sal-dach)]-Y (d).

On the basis of all these studies, the structures as shown in Scheme 3.2 have been proposed for these complexes.

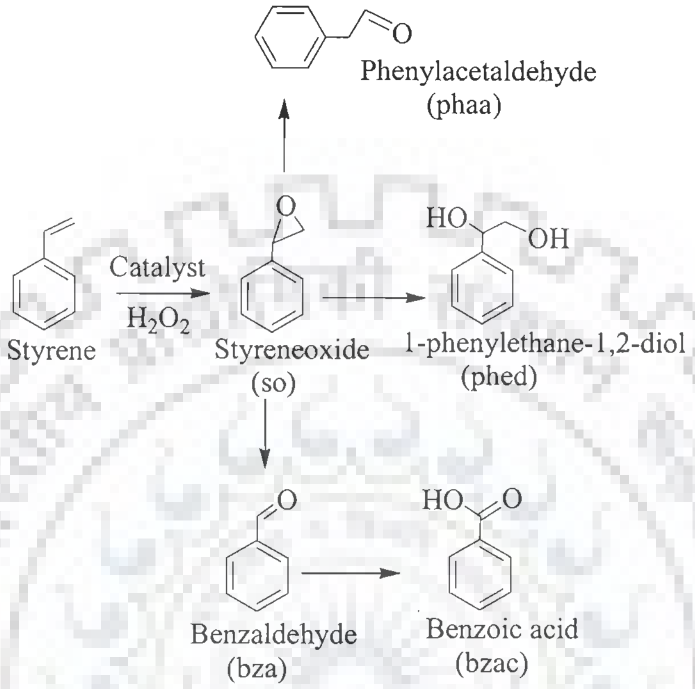


Scheme 3.2: Proposed structures for complexes

3.3.7. Catalytic activity studies

3.3.7.1. Oxidation of styrene

The oxidation of styrene, catalysed by [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y was carried out using H_2O_2 as an oxidant to give styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenyl acetaldehyde along with only minor amounts of unidentified products. The formation of all these products is represented by Scheme 3.3. These are common products and have been identified by others as well [128, 142, 153].



Scheme 3.3: Various oxidation products of styrene

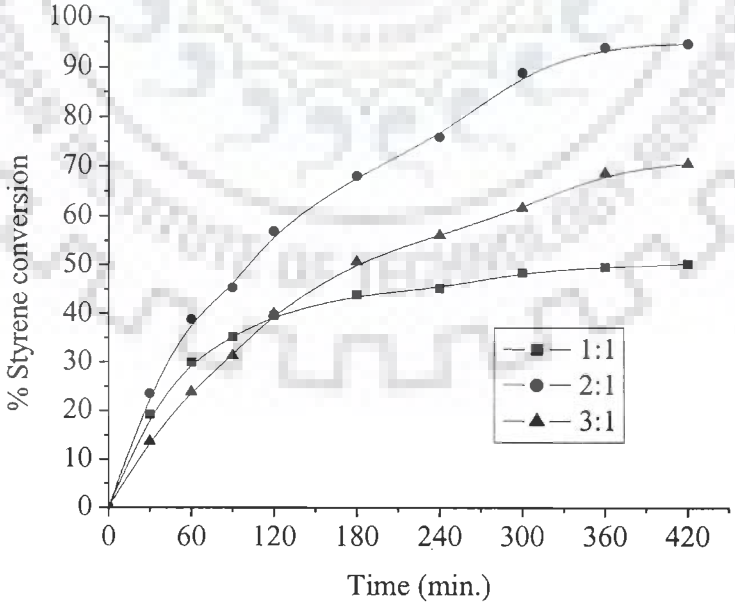


Figure 3.6. Effect of H_2O_2 concentration (H_2O_2 : styrene) on oxidation of styrene.

In search of suitable reaction conditions to achieve the maximum oxidation of styrene, the effect of three different reaction parameters viz. oxidant concentration, catalyst concentration and temperature of the reaction were studied.

The effect of H_2O_2 concentration on the oxidation of styrene is illustrated in Figure 3.6. Three different H_2O_2 / styrene molar ratios 1:1, 2:1 and 3:1 were considered while keeping the fixed amount of styrene (1.04 g, 10 mmol) and catalyst (0.025 g) in 20 ml of CH_3CN at 80 °C. Increasing the H_2O_2 / styrene ratio from 1:1 to 2:1 increases the conversion from 65.6 % to 94.6 %. Further increasing the ratio to 3:1, though, speeds up the initial conversion but over all conversion rolls back to 70.4 %. The reason for this may be due to the dilution of the reaction mixture by the presence of larger amount of water molecules in H_2O_2 solution. It is, therefore, concluded that the 2:1 molar ratio is best one to obtain the maximum styrene conversion of 94.6 % in 7 h reaction time. The effect of amount of catalyst on the oxidation of styrene was also studied. Five different amounts of [VO(sal-dach)]-Y viz. 0.015, 0.020, 0.025, 0.035 and 0.050 g were considered while keeping fixed amounts of styrene (1.04 g, 10 mmol) and H_2O_2 (2.28 g, 20 mmol) in 20 ml of CH_3CN and the reaction was carried out at 80 °C. As illustrated in Figure 3.7, the conversion increases on increasing the amount of catalyst and a maximum of 94.6 % conversion has been achieved with 0.025 g of catalyst. A further increase in catalyst amount of catalyst amount results in lower conversion. Therefore, an amount of 0.025 g catalyst may be considered as an optimum to obtain the maximum conversion of styrene. Figure 3.8 illustrates the effect of oxidation of styrene at different temperatures. Amongst the four different temperatures of 50, 60, 70 and 80 °C, the reaction at 80 °C keeping the other conditions optimised as above gave the highest conversion of 94.6 %. A total of 7 h was required to obtain equilibrium. Thus, for the maximum oxidation of 10 mmol of styrene other required reagents as concluded were: [VO (sal-dach)]-Y (0.025 g), H_2O_2 (2.28 g, 20 mmol) in CH_3CN (20 ml) and temperature (80 °C).

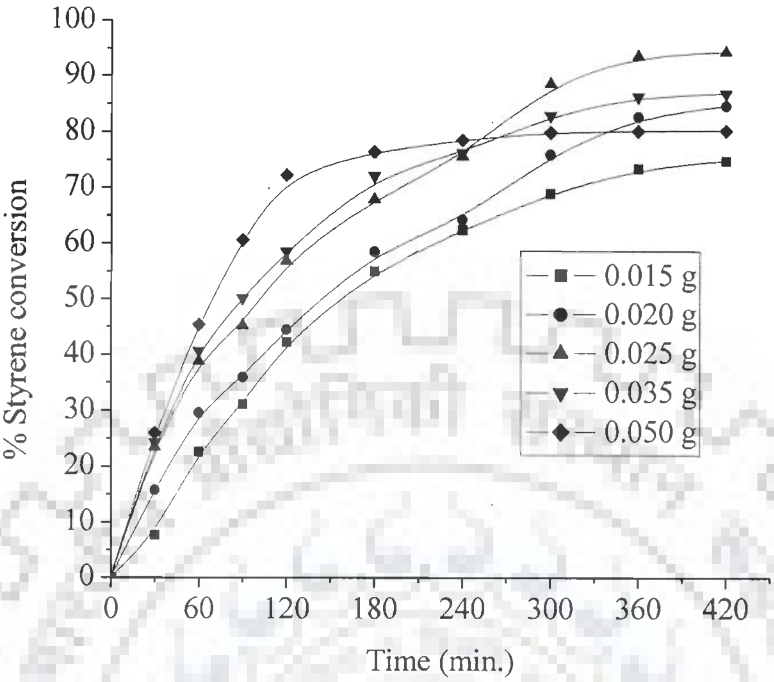


Figure 3.7. Effect of amount of catalyst on the oxidation of styrene.

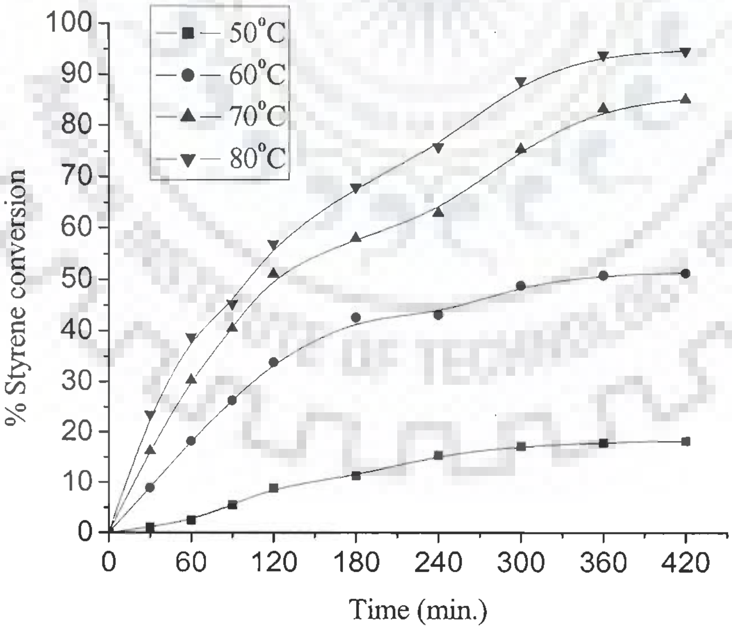


Figure 3.8. Effect of temperature on the oxidation of styrene.

Under these optimized reaction conditions, catalyst [Cu(sal-dach)]-Y has shown a maximum of only 21.7 % conversion after 7 h of reaction time with four reaction products: styreneoxide, benzoic acid, benzaldehyde and phenyl acetaldehyde while, as mentioned earlier, [VO(sal-dach)]-Y has given one additional product, 1-phenylethane-1,2-diol. Table 3.3 compares their selectivity data along with the conversion percentage and turn over frequency (TOF) after 7 h of reaction time. It is clear from the data that the selectivity of the various products obtained from catalyst [VO(sal-dach)]-Y follow the order: benzaldehyde (54.5 %) > 1-phenylethane-1,2-diol (22.5 %) > benzoic acid (8.9 %) > styrene oxide (7.6 %) > phenyl acetaldehyde (4.9 %). Catalyst [Cu(sal-dach)]-Y gave slightly different selectivity order. Here, the selectivity of styrene oxide is better (12.9 %) while the highest selectivity of benzaldehyde (67.3 %) is maintained. Catalytic activity of neat complexes [VO(sal-dach)] and [Cu(sal-dach)] have also been tested. Figure 3.9 presents the profiles of conversion percentage of styrene as a function of time for these catalysts including their encapsulated analogues. Neat complexes also exhibit good catalytic activity. This is due to the presence of more number of metal centres in homogeneous catalyst than heterogeneous one within the same weight of catalyst. The yields of various reaction products are also very much similar to their encapsulated analogues. However, the turns over frequencies are extremely low as compared to their encapsulated analogues.

Table 3.3. Products selectivity and percent conversion of styrene after 7 h of reaction time

Catalyst (0.025 g)	% Conv.	TOF $(h^{-1})^a$	% Product selectivity[b]					
			so	bza	phed	bzac	phaa	Others
[VO(sal-dach)]-Y	94.6	327.5	7.6	54.2	22.5	8.9	4.9	1.9
[Cu(sal-dach)]-Y	21.7	30.1	12.9	67.3	-	7.1	12.0	0.8
[VO(sal-dach)]	39.4	8.7	3.9	69.0	16.2	5.2	0.6	0.9
[Cu(sal-dach)]	31.8	6.9	13.8	58.4	-	12.9	13.1	0.8

[a] TOF h^{-1} (Turnover frequency): moles of substrate converted per mole of metal ion (in the solid state catalyst) per hour

[b] For abbreviations see Scheme 3.3

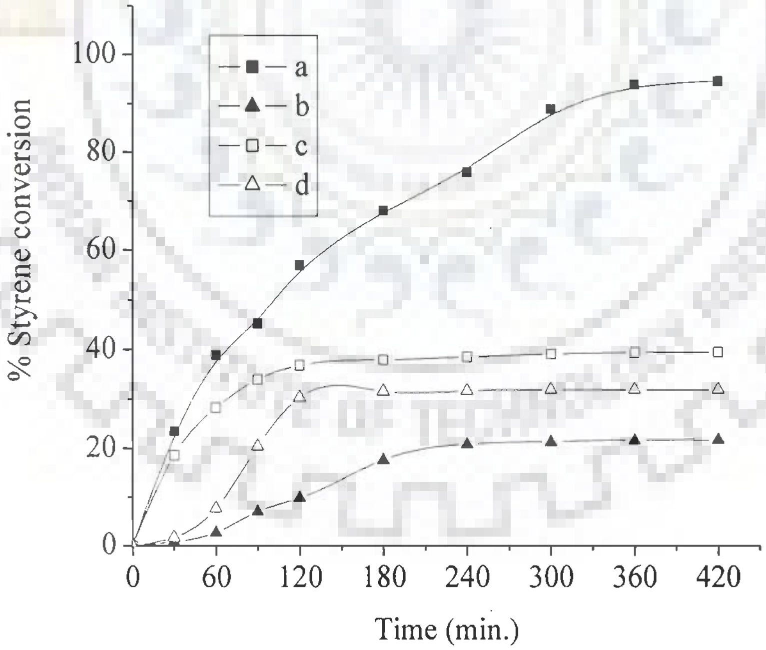
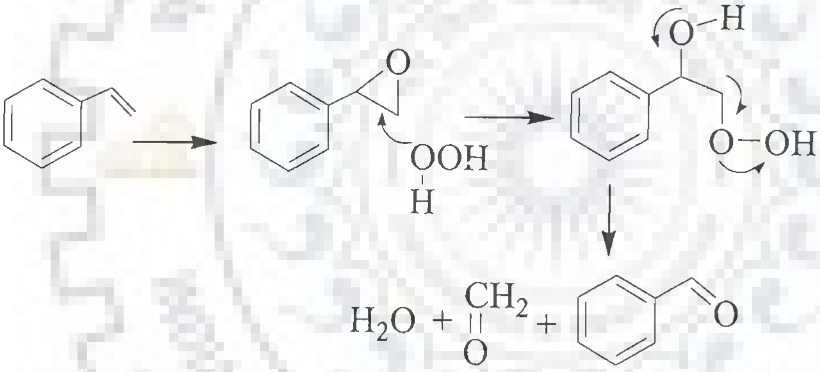


Figure 3.9. Catalytic comparison of catalysts for the oxidation of styrene: [VO(sal-dach)]-Y(a), [Cu(sal-dach)]-Y(b), [VO(sal-dach)] (c) and [Cu(sal-dach)] (d).

A highest yield of benzaldehyde is possibly due to further oxidation of styreneoxide formed in the first step by a nucleophilic attack of H_2O_2 on styrene oxide followed by cleavage of the intermediate hydroperoxistyrene; Scheme 3.4 [6]. Similarly, the formation of phenylacetaldehyde is possible through the isomerisation of styreneoxide. The presence of styreneoxide in low percentage is thus likely. The formation of benzaldehyde may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via a radical mechanism. High amount of water present in H_2O_2 is partly responsible for the possible hydrolysis of styreneoxide to 1-phenylethane-1,2-diol. Other products e.g. benzoic acid formation is possible due to further oxidation of benzaldehyde.

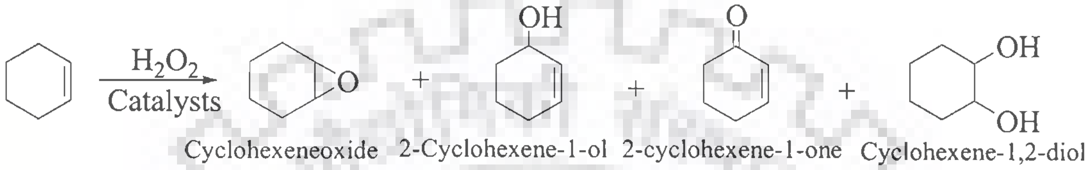


Scheme 3.4

Catalytic potential of these complexes can not be compared directly with similar complexes due to limited literature. About 34.8 % conversion of styrene was noted with zeolite-Y encapsulated [VO(salphen)] using 70% tert-butylhydroperoxide as an oxidant [128]. Zeolite-Y encapsulated catalyst [Mn(salen)]-Y exhibits ca. 30 % conversion of styrene using molecular oxygen as an oxidant in excess of *tert*-butylhydroperoxide as initiator [153]. About 80 % conversion of styrene was noted with polymer supported catalyst PS-K[VO_2(sal-ohyba)] (H_2sal-ohyba = Schiff base derived from salicylaldehyde and *o*-hydrobenzylamine) [6].

3.3.7.2. Oxidation of cyclohexene

Complexes [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y catalyze the oxidation of cyclohexene by H_2O_2 efficiently to give cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as presented in Scheme 3.5. Reaction conditions have also been optimized for the maximum oxidation of cyclohexene by varying different parameters.



Scheme 3.5

Three different cyclohexene:30 % aqueous H_2O_2 molar ratios viz. 1:1, 1:2 and 1:3 were considered while keeping the fixed amounts of cyclohexene (0.82 g, 10 mmol) and catalyst (0.025 g) in 20 ml of MeCN and reaction was carried out at 75 °C. The percentage conversions noted at various times are presented in Figure 3.10. A maximum of 52.8 % conversion was noted for the cyclohexene to H_2O_2 ratio of 1:1 in 6 h of reaction time. This conversion reached to 68.3 % at a cyclohexene to H_2O_2 molar ratio of 1:2. Increasing cyclohexene:H_2O_2 ratio further to 1:3 results in only 48.0 % conversion of cyclohexene. This is possibly due to the presence of excess water as has been noted earlier also. Thus, a large amount of oxidant is not an essential condition to maximize the oxidation.

The effect of amount of catalyst on the oxidation of cyclohexene is shown in Figure 3.11. Three different amounts of catalyst viz. 0.015, 0.025 and 0.035 g were considered while keeping other conditions as above. It is clear from the plot that 0.035 g catalyst amount is the best one to obtain the highest (86.6 %) cyclohexene conversion. The oxidation of cyclohexene is also a strong function of reaction temperature. As shown in Figure 3.12, amongst three temperatures of 55, 65 and 75 °C, a maximum of 86.6 % conversion of cyclohexene was obtained at 75 °C. Thus, optimized conditions for the oxidation of 10 mmol of cyclohexene were fixed as follow: 0.035 g catalyst, 20 mmol 30 % aqueous H_2O_2, 20 ml CH_3CN and 75 °C reaction temperature.

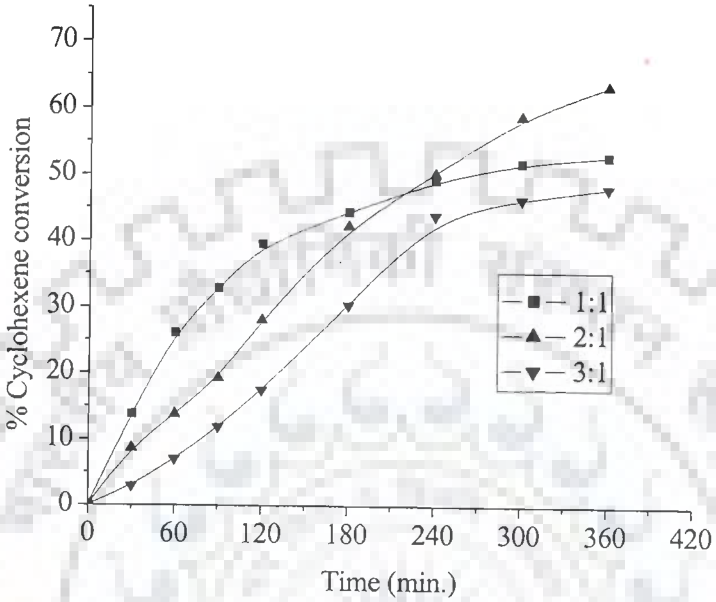


Figure 3.10. Effect of H_2O_2 concentration (cyclohexene : H_2O_2 molar ratio) on the oxidation of cyclohexene.

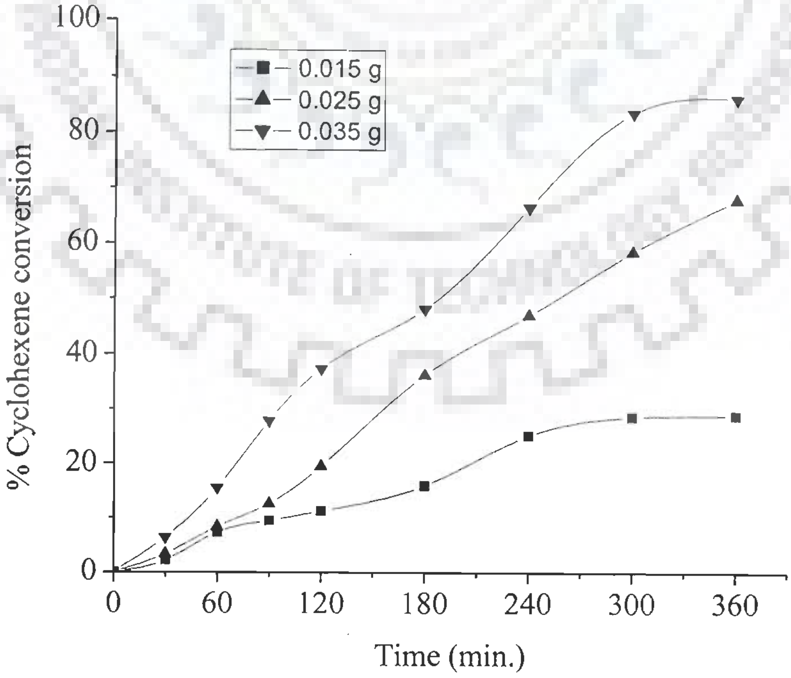


Figure 3.11. Effect of amount of catalyst on the oxidation of cyclohexene.

Catalytic activities of these complexes have been compared only with similar complexes. Thus, polymer supported catalysts [–CH_2{VO(sal-dach)·DMF}–$]_n$ ([–CH_2(H_2sal-dach)–$]_n$ = polymeric ligand derived from 5,5′-methylenebis(salicylaldehyde) and 1,2-diaminocyclohexane) and [–S_2{VO(sal-dach)·DMF}–$]_n$ ([–S_2(H_2sal-dach)–$]_n$ = 5,5′-dithiobis(salicylaldehyde) and 1,2-diaminocyclohexane) with very similar ligands exhibit 98 % conversion of cyclohexene using *tert*-butylhydroperoxide as an oxidant and are much better than both the catalysts reported here [123].

Neat complexes [VO(sal-dach)] and [Cu(sal-dach)] exhibit 42.6% and 23.5% conversion, respectively, and thus have good catalytic activity. The order of the selectivity of reaction products is also same as observed for their encapsulated analogues. Again, the formation of cyclohexeneoxide in both cases is extremely low. Table 4 presents data for neat as well as encapsulated complexes. The calculated turn over frequency in both cases is low (7.8 for [VO(sal-dach)] and 4.3 for [Cu(sal-dach)]) as compared to encapsulated complexes (249.9 for [VO(sal-dach)] and 21.0 for [Cu(sal-dach)]). Thus, turn over frequency as well as other characteristics, such as, stability, recycle ability and operational flexibility make the encapsulated catalysts better over neat complexes.

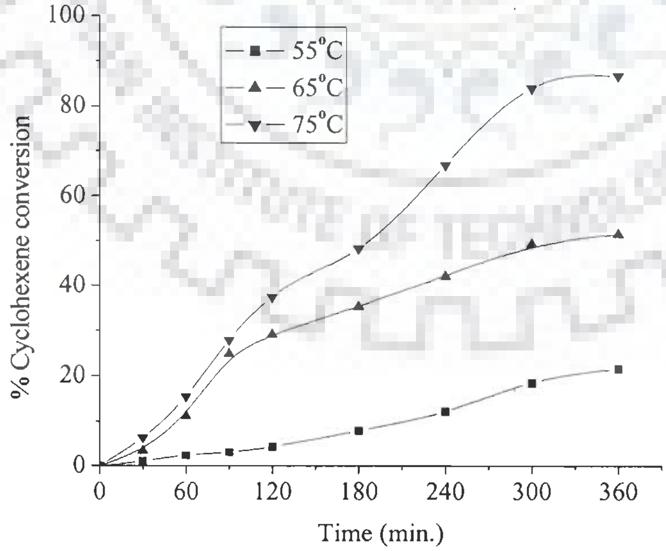


Figure 3.12. Effect of temperature on the oxidation of cyclohexene.

Under the optimized reaction conditions catalyst [Cu(sal-dach)]-Y has shown only 18.1 % conversion suggesting its poor catalytic ability. The oxidation products identified with this catalyst were cyclohexeneoxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one while one more product cyclohexane-1,2-diol was noted in case of [VO(sal-dach)]. Figure 3.13 presents the conversion details as a function of time while Table 3.5 lists products selectivity along with the conversion and turn over frequency for these catalysts. The selectivity order for the catalyst [VO(sal-dach)] is: 2-cyclohexene-1-one (53.1 %) > 2-cyclohexene-1-ol (27.9 %) > cyclohexane-1,2-diol (10.4 %) > cyclohexeneoxide (5.0 %) and for [Cu(sal-dach)] is: 2-cyclohexene-1-ol (49.2 %) > 2-cyclohexene-1-one (32.0 %) > cyclohexeneoxide (18.8 %). Thus, in terms of the selectivity of cyclohexeneoxide, [Cu(sal-dach)]-Y is better than [VO(sal-dach)]-Y (18.8 % versus 5.0 %), though formation of cyclohexeneoxide is not very encouraging in both cases.

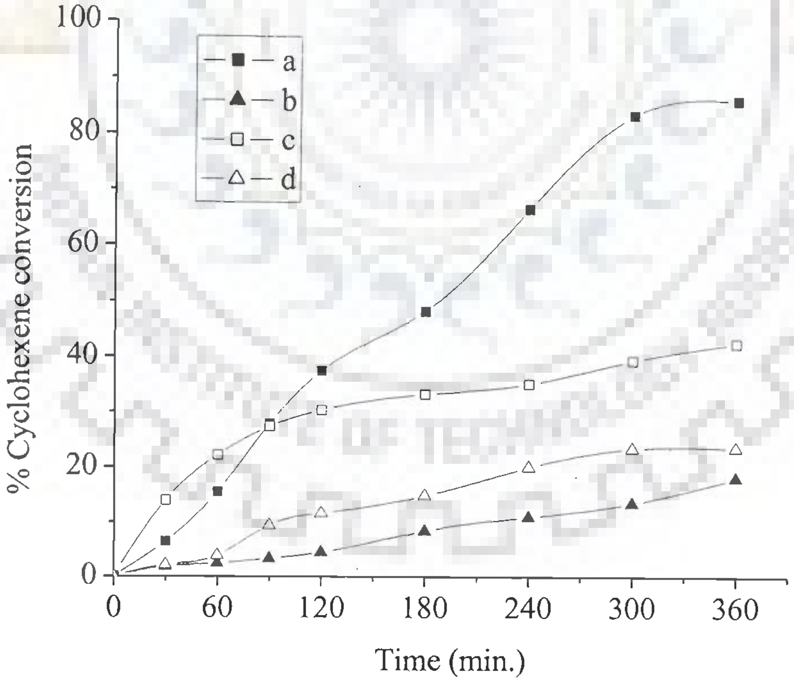
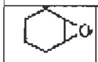
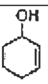
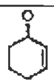
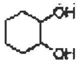


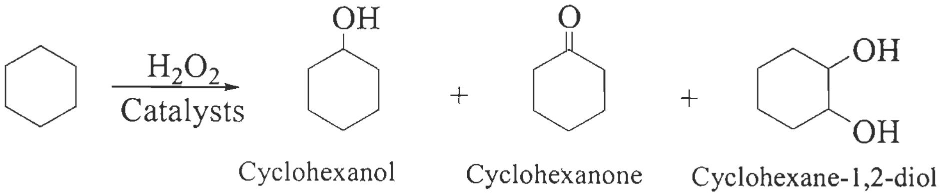
Figure 3.13. Effect of catalysts, [VO(sal-dach)]-Y(a), [Cu(sal-dach)]-Y(b), [VO(sal-dach)] (c) and [Cu(sal-dach)] (d) on the oxidation of cyclohexene.

Table 3.4. Effect of different catalysts on the oxidation of cyclohexene and product selectivity

Catalyst	% Conv.	TOF (h^{-1})	% Product selectivity				
							Others
[VO(sal-dach)]-Y	86.6	249.9	5.0	27.9	53.1	10.4	3.5
[Cu(sal-dach)]-Y	18.1	21.0	18.8	49.2	32.0	-	-
[VO(sal-dach)]	42.6	7.8	7.7	34.4	44.2	5.3	8.4
[Cu(sal-dach)]	23.5	4.3	10.9	45.7	39.4	2.2	1.8

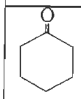
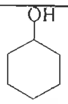
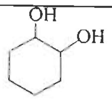
3.3.7.3. Oxidation of cyclohexane

The applicability of synthesized catalyst have also explored towards oxidation of cyclohaxane under the operating conditions optimized for cyclohexene. Thus, 20 mmol 30 % H_2O_2, 0.035 g catalyst and 20 ml CH_3CN were considered for 10 mmol of cyclohexane and reaction was carried out at 70 °C. Under these reaction conditions, catalysts [Cu(sal-dach)]-Y and [VO(sal-dach)]-Y gave 78.1 and 21.0 % conversion, respectively, of cyclohexane with major reaction products of cyclohexanone, cyclohexanol and cyclohexane-1,2-diol as shown in Scheme 3.6. About 2 h was required to achieve equilibrium in these reactions. Amongst the various products formed, the selectivity of cyclohexanol was found to be highest (82.2 % for [Cu(sal-dach)]-Y and 93.3 % for [VO(sal-dach)]-Y) while selectivities of other two products were much less. Neat complexes have also shown relatively good catalytic activity. However, the TOF values, as noted in other cases, are high and are 190 for [Cu(sal-dach)]-Y and 127.2 for [VO(sal-dach)]-Y. All these details are presented in Table 3.5.



Scheme 3.6

Table 3.5. Effect of different catalysts on the oxidation of cyclohexane and product selectivity

Catalyst	% Conv.	TOF (h^{-1})	% Product selectivity			
						Others
[VO(sal-dach)]-Y	78.1	190.0	4.8	82.2	8.7	4.3
[Cu(sal-dach)]-Y	21.0	127.2	2.0	91.2	4.7	2.1
[VO(sal-dach)]	36.8	14.1	2.4	93.1	3.2	1.3
[Cu(sal-dach)]	40.9	15.8	1.8	90.3	1.5	6.4

Catalytic potential of these complexes has been compared indirectly due to limited literature. Neat [Cu(salen)] exhibits only 18% conversion of cyclohexene [160]. Other catalysts have shown comparable catalytic activities [162, 163].

3.3.8. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the methanolic solution of neat complexes was treated with 30 % H_2O_2 dissolved in methanol and the progress of the reaction was monitored by electronic absorption spectroscopy. Thus, the titration of ca. 10^{-4} M methanolic solution of [VO(sal-dach)] with one-drop portions of 30% H_2O_2 dissolved in methanol resulted in decrease in the band maximum at 360 nm, while the intensity of UV band at 277 nm slowly increases with marginal shift and appears as a broad band; Figure 3.14. The weak broad band appearing at 568 nm slowly decreases its intensity and finally disappears (see inset of Figure 3.14). All these suggest the interaction of H_2O_2 with oxovanadium(IV) centre to give oxoperoxovanadium(V) species. Similar results have also been noted earlier when [VO(sal-dach)] was titrated with tert-butylhydroperoxide [123]. Such peroxo species is responsible for the transfer of oxygen atom to the substrates. However, no change in the IR as well as electronic spectral features of the recovered encapsulated complex after first cycle of all catalytic reactions and drying after washing with acetonitrile suggest that the oxidized species acquires its original state and exists as [VO(sal-dach)].

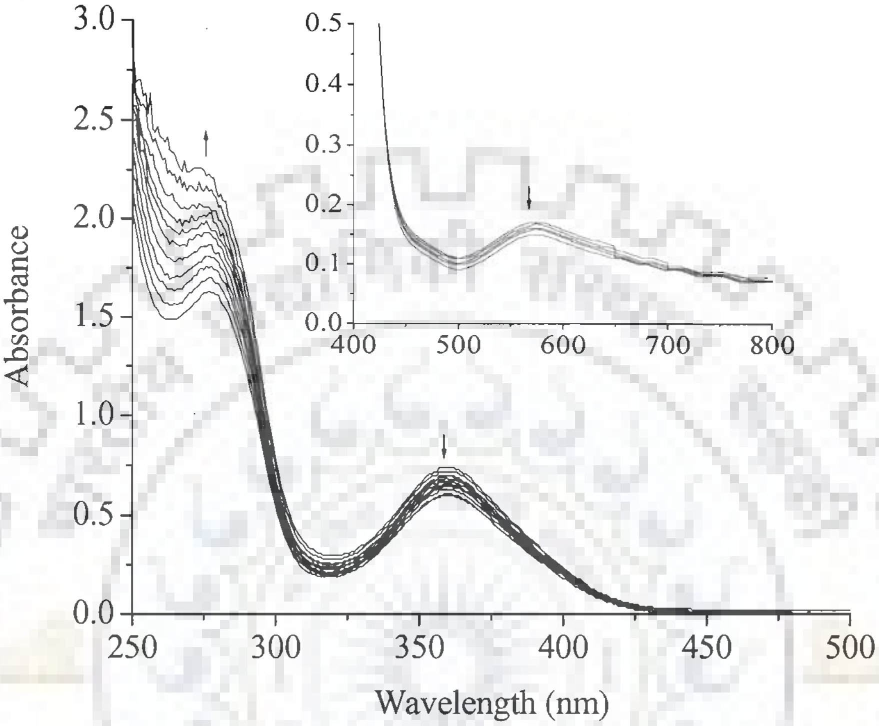


Figure 3.14. Titration of [VO(sal-dach)] with 30 % H_2O_2. The spectra were recorded after successive addition of one drop portions of H_2O_2 to 10 ml of ca. 10^{-4} M solution of [VO(sal-dach)] in methanol.

Similarly, the titration of ca. 10^{-4} mol methanolic solution of [Cu(sal-dach)] with one-drop portions of 30 % H_2O_2 dissolved in methanol resulted in decrease in the band maximum at 561 nm without changing its position. At the same time the band at 357 nm experiences only slight increase in intensity while 273 nm band gradually shifts to 266 nm along with the increase in band maximum and finally disappears. Figure 3.15 presents all these spectral changes observed. Again, these changes suggest the interaction of H_2O_2 with Cu(II) centre.

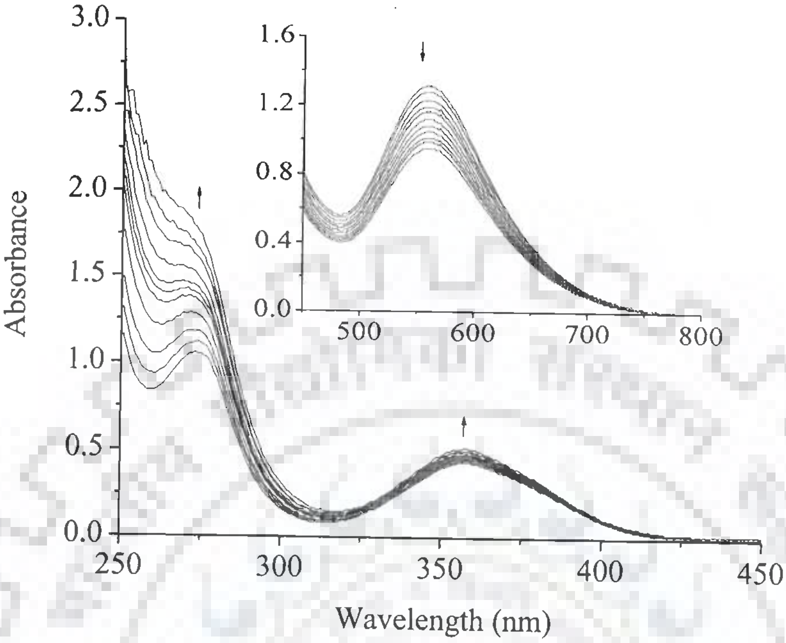


Figure 3.15. Titration of [Cu(sal-dach)] with H_2O_2. The spectra were recorded after successive addition of one drop portions of H_2O_2 to 10 ml of ca. 10^{-4} M solution of [Cu(sal-dach)] in methanol.

At least three types of intermediates having copper-oxygen interaction viz. side-on Cu^{III}–(μ-η^2–peroxo)–Cu^{III}, bis(μ–oxo–Cu^{III}) and Cu^{III}–O–O–H (copper-hydroperoxide) have been reported in the literature during catalytic action [154, 155]. A monomeric copper-hydroperoxide species formation may be expected in the zeolite encapsulated copper(II) complex. Hydroperoxocopper complexes are known to exhibit a charge transfer band at ca. 600 nm [156]. The decrease in intensity of 561 nm band without any isosbestic point in neat complex may possibly be due to the merging of this additional charge transfer band with d-d transition. Such in situ generated intermediate species finally transfers coordinated oxygen atoms to the substrates to give products. Thus, the catalytic performance of encapsulated catalyst could be attributed to the formation of facile and reversible intermediate species.

3.5. CONCLUSIONS

Complexes [VO(sal-dach)] and [Cu(sal-dach)] have been encapsulated in the super cages of zeolite-Y and their encapsulation has been ensured by different studies. These complexes have potential catalytic activities for the oxidation of styrene, cyclohexene and cyclohexane. Reaction conditions have been optimized considering different parameters to get maximum conversion of these substrates. A maximum of 94.6 % conversion with five different oxidation products of styrene has been obtained with [VO(sal-dach)]-Y. The selectivity of these products follows the order: benzaldehyde (54.5 %) > 1-phenylethane-1,2-diol (22.5 %) > benzoic acid (8.9 %) > styrene oxide (7.6 %) > phenyl acetaldehyde (4.9 %). With four products having selectivity order: benzaldehyde (69.0 %) > styreneoxide (12.9 %) > phenyl acetaldehyde (12.0 %) > benzoic acid (7.1 %), [Cu(sal-dach)]-Y gave only 12.7 % conversion. With 86.6 % conversion of cyclohexene for [VO(sal-dach)]-Y, the selectivity of four different products follow the order: 2-cyclohexene-1-one (53.1 %) > 2-cyclohexene-1-ol (27.9 %) > cyclohexane-1,2-diol (10.4) > cyclohexeneoxide (5.0 %). [Cu(sal-dach)]-Y gave only 18.1 % conversion and only three products have been obtained with the following order of selectivity: 2-cyclohexene-1-ol (49.2 % %) > 2-cyclohexene-1-one (32.0 %) > cyclohexeneoxide (18.8 %). This order of catalytic activity is reverse during the oxidation of cyclohexane. A maximum of 78.1 % of cyclohexane with [Cu(sal-dach)]-Y and only 21.0 % with [VO(sal-dach)-Y has been obtained where selectivity of three major products follows the order: cyclohexanol > cyclohexane-1,2-diol > cyclohexanone. Generally vanadium based catalyst is more active than copper based catalyst and is interpreted due the readily formation of peroxo complex and transferring the oxygen to the substrates. These complexes are stable and do not leach during the catalytic reaction as have been confirmed by testing the filtrate for the corresponding metal ion and thus suggest their heterogeneous nature. The high turn over frequencies of the complexes make them suitable catalysts for these catalytic oxidations.

CHAPTER-4

Zeolite encapsulated metal complexes of vanadium(VI), copper(II) and nickel(II) as catalyst for the oxidation of styrene, cyclohexane and methyl phenyl sulfide

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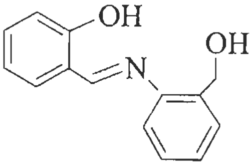
4.1. INTRODUCTION

Transition metal complexes are well known for their catalytic activities in the oxidation as well as reduction of organic substrates and for the synthesis of a number of fine chemicals. Their immobilizations on solid supports provide certain additional characteristic properties such as selectivity, thermal stability, easy separation from the reaction mixture and recycle ability [8, 12, 13, 164]. The immobilized materials are important to develop new environment friendly technologies. Immobilization of metal complexes in the nano cavity of zeolite is often termed as "zeolite encapsulated metal complexes" (ZEMC). Encapsulated molecules in zeolite are free to move within the cavity of zeolite [157]. These zeolite encapsulated metal complexes have been suggested as model compounds for enzyme mimicking and often referred to as "zeozymes" [15]. The advantages of immobilized metal complexes promoted several research groups to investigate the catalytic properties of the complexes entrapped within the nano-cavities of zeolite-Y [36, 37, 91, 97, 128, 165].

In this paper, we report the encapsulation of oxovanadium(IV), copper(II) and nickel(II) complexes of Schiff bases derived from salicylaldehyde and *o*-aminobenzylalcohol (H_2sal-oaba, **4.I**; Scheme 4.1) in nano cavities of zeolite-Y by the flexible ligand method. These zeolite encapsulated metal complexes have been screened for the oxidation of styrene, cyclohexane and thioanisole. Suitable reaction conditions have been optimized to obtain maximum oxidation of organic substrates. As neat copper(II) and oxovanadium(IV) complexes have tendency to stabilize as dinuclear [166, 167], encapsulation in the cavity of zeolite prevent their dimerisation and allow their stabilization as monomeric active centre.



I: H_2sal-oaba

Scheme 4.1

4.2. EXPERIMENTAL

4.2.1. Materials and methods

Analytical reagent grade cyclohexane, 30 % aqueous H_2O_2 (Ranbaxy, India), styrene (Acros Organics, New Jersey, USA), methyl phenyl sulfide (Alfa Aeaser, USA), 2-aminobenzyl alcohol (Aldrich Chemical Company, USA), salicylaldehyde (sal), cupric nitrate, nickel nitrate, cupric acetate monohydrate, nickel acetate tetra hydrate (E. Merck, India) and vanadyl sulfate penta hydrate (Loba Chemie, India) were used as obtained. Na-Y zeolite (Si/Al ~ 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were of AR grade. Instrumentation and analyses details are given in Chapter- 2.

4.2.2. Preparations

4.2.2.1. Preparation of H_2sal-oaba (4.I)

Ligand H_2sal-oaba was prepared following the literature procedure [166]. A mixture of 2-aminobenzylalcohol (1.23 g, 10 mmol) and salicylaldehyde (1.22 g, 10 mmol) was taken in methanol (50 ml) and the reaction mixture was heated under reflux on a water bath for 1 h. After cooling to room temperature, the yellow precipitate of **I** was filtered, washed with methanol and dried in vacuum. Yield: 72%. ^{1}H NMR (δ in ppm): 13.08 (s, 1H), 8.66 (s, 1H), 6.83-7.75 (m, 8H) and 4.57 (s, 2H).

4.2.2.2. Preparation of M-Y (M = Cu(II), Ni(II) and OV(IV))

An aqueous solution of metal nitrate [nitrates of Cu(II) and Ni(II)] or vanadyl sulfate (12 mmol in 50 ml) was added to a suspension of Na-Y zeolite (5.0 g) in 250 ml of distilled water and the mixture was stirred at 90 °C for 24 h. The light colour solid was filtered, washed with hot distilled water until filtrate was free from any metal ion content, and dried at 120 °C in air oven for 24 h.

4.2.2.3. Preparation of [VO^{IV}(sal-oaba)(H_2O)]-Y (4.1)

Ligand, H_2sal-oaba (2.5 g) and OV(IV)-Y (1.0 g) were mixed in 50 ml of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was separated by filtration and then extracted with methanol using Soxhlet extractor to remove unreacted ligand from the cavities of the zeolite as well as located on the surface of the zeolite along with neat complexes, if any. The unreacted oxovanadium(IV) ions present in the zeolite was removed by stirring with aqueous 0.01 M NaCl solution (200 ml) for 8 h. The resulting solid was filtered and washed with distilled water until free from chloride ions. Finally, it was dried at 120 °C in an air oven for several hours.

4.2.2.4. Preparation of Cu^{II}(sal-oaba)(H_2O)]-Y (4.2) and [Ni^{II}(sal-oaba)(H_2O)$_3$]-Y (4.3)

Complexes [Cu^{II}(sal-oaba)(H_2O)]-Y **(4.2)** and [Ni^{II}(sal-oaba)(H_2O)$_3$]-Y **(4.3)** were prepared following essentially the same procedure out lined for [VO(sal-oaba)(H_2O)]-Y by replacing OV(IV)-Y with Cu(II)-Y or Ni(II)-Y.

4.2.2.5. Preparation of [VO^{IV}(sal-oaba)])(4.4)

A stirred solution of H_2sal-oaba (1.355 g, 5 mmol) in dry methanol (50 ml) was treated with [VO(acac)$_2$] (1.33 g, 5 mmol) dissolved in dry methanol (25 ml) and the resulting reaction mixture was refluxed in an oil bath for 2 h. After cooling down to room temperature over night, a greenish precipitate of **4.4** was filtered off, washed with methanol and dried in vacuum over silica gel. Yield: 80 %.

4.2.2.6. Preparation of [Cu(sal-oaba)](4.5) and [Ni(sal-oaba)(H_2O)$_3$] (4.6)

Complexes [Cu(sal-oaba)](**4.5**) [167] and [Ni(sal-oaba)(H_2O)$_3$] (**4.6**) [168] were prepared as described in the literature. A stirred solution of H_2sal-oaba (1.355 g, 5 mmol) in methanol (50 ml) was added to a filtered solution of respective metal acetate (5 mmol) in methanol (50 ml) and the resulting reaction mixture was refluxed on a water bath for 4 h. After reducing the solvent volume to ca. 40 ml, the flask was kept at ambient temperature for over night where coloured mass separated out in both cases. These were filtered, washed with methanol and dried in vacuum over silica gel. Yield: ca. 60 %.

4.2.3. Catalytic activity studies

4.2.3.1. Oxidation of styrene

The catalytic oxidation of styrene was carried out in a 50 ml two necked flask fitted with septum and water circulated condenser using a general procedure for all catalysts. In a typical reaction, an aqueous 30 % H_2O_2 or 70 % *tert*-butylhydroperoxide (TBHP) (20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH_3CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The encapsulated catalyst (0.025 g) was added to the reaction mixture and the reaction was considered to begin. During the reaction, the products were analysed (by withdrawing small aliquots after specific interval of time) using a gas chromatograph. The identities of the products were confirmed by GC-MS.

4.2.3.2. Oxidation of cyclohexane

Aqueous 30% H_2O_2 (2.28 g, 20 mmol), cyclohexane (0.84 g, 10 mmol) and catalyst (0.040 g) were mixed in 5 ml of CH_3CN and the reaction mixture was heated at 70 °C with continuous stirring in an oil bath for 2 h. The reaction products were analysed using gas chromatograph as mentioned above.

4.2.3.3. Oxidation of methyl phenyl sulfide (thioanisol)

Aqueous 30 % H_2O_2 (0.57 g, 5 mmol), thioanisol (0.62 g, 5 mmol) and catalyst (0.015 g) were mixed in 20 ml of CH_3CN and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored as mentioned above and the identities of various products were confirmed by GC-MS.

4.3. RESULTS AND DISCUSSION

4.3.1. Characterization of catalysts

Encapsulation of complexes, $[VO^{IV}(sal\text{-}oaba)(H_2O)]$, $[Cu^{II}(sal\text{-}oaba)(H_2O)]$ and $[Ni^{II}(sal\text{-}oaba)(H_2O)_3]$ in the nano cavity of zeolite-Y was carried out by flexible ligand method where ligand enters slowly into the cavity through the zeolite pores due to its flexible nature and reacts with previously exchanged metal ions. The resulting complexes are big enough in size and do not escape from the nano cavity of zeolite. The purification of crude mass by Soxhlet extraction using excess of methanol removed free ligand that remained uncomplexed in the cavities of the zeolite along with the neat complex formed on the surface of the zeolite, if any. The uncomplexed metal ions remained, if any, in the cavity of zeolite were removed by exchanging back with aqueous 0.01 M NaCl solutions. The percentages of metal contents determined before and after encapsulation by inductively coupled plasma along with their expected formula and color are presented in Table 4.1. As crude mass was extracted with methanol, the metal ion content found after encapsulation is only due to the presence of metal complexes in the super cages of the zeolite-Y.

Neat complexes [VO(sal-oaba)], [Cu(sal-oaba)] and $[Ni(sal\text{-}oaba)(H_2O)_3]$ have also been prepared by reacting H_2sal-oaba with suitable metal precursors. These complexes have previously been prepared and well characterised [166-168]. The dimeric square pyramidal structure for [VO(sal-oaba)], dimeric square planar structure for [Cu(sal-oaba)] and monomeric octahedral structure for [Ni(sal-oaba)(H_2O)$_3$] have been reported. A detailed spectroscopic study (IR and electronic) for these complexes has, therefore, been only considered to compare their properties with the corresponding encapsulated complexes. As encapsulated complexes can not dimerise in the cavity of zeolite, a monomeric species with coordinated water molecule(s) to complete the coordination geometry is expected.

Table 4.1. Chemical composition, physical and analytical data

No.	Catalyst	Colour	Metal content (wt %)
1	OV(IV)-Y	Light green	4.6
2	Cu(II)-Y	Pale blue-green	7.6
3	Ni(II)-Y	Pale-green	6.8
4	[VO(sal-oaba)(H_2O)]-Y	Light green	2.6
5	[Cu(sal-oaba)(H_2O)]-Y	Light green	3.3
6	[Ni(sal-oaba)(H_2O)$_3$]-Y	Yellow	1.5

4.3.2. Scanning electron micrograph studies

The scanning electron micrographs (SEM) of OV(IV)-Y, Cu(II)-Y and Ni(II)-Y, and their respective metal complexes were recorded to observe the morphological changes and crystallinity of materials. Figure 4.1 presents the representative micrographs. It is clear from the micrographs that metal exchanged zeolites as well as zeolites having metal complexes entrapped have well defined crystal and there is no indication of the presence of any metal ions or complexes on the surface. It has not been possible to see any morphological changes on the surface on encapsulation of the complexes in the cavity possibly due to their poor loading.

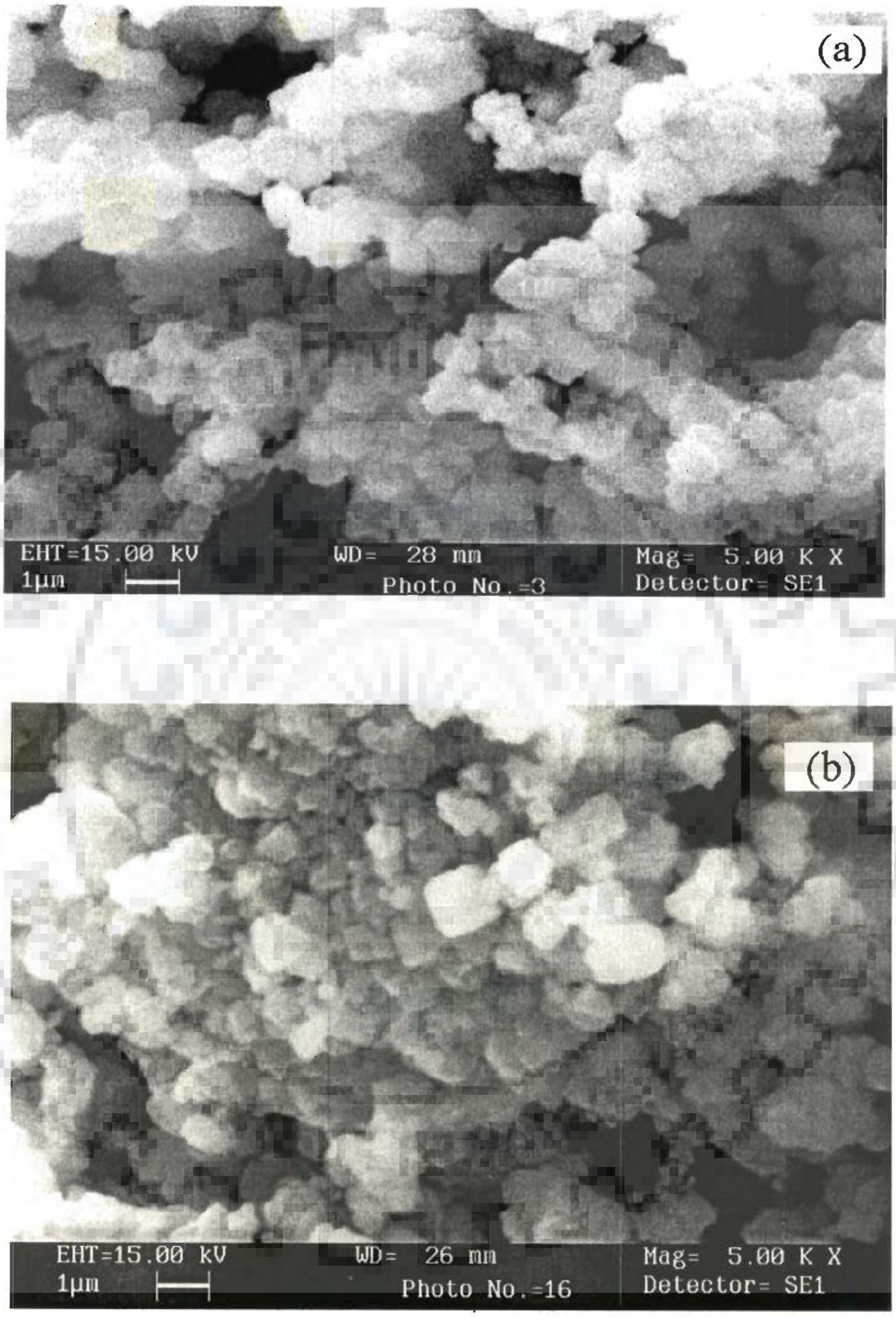


Figure 4.1. Scanning electron micrograph of (a) Cu-Y and (b) [Cu (sal-oaba)]-Y.

4.3.3. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na–Y, M–Y (M = OV(IV), Cu(II) and Ni(II)) and encapsulated metal complexes were recorded at 2θ values between 5 and 70°. The XRD patterns of representative metal exchanged zeolite and zeolite encapsulated metal complexes along with Na-Y are presented in Figure 4.2. The diffraction patterns of encapsulated metal complexes, M–Y and Na–Y are essentially similar except a slight change in the intensity of the bands in encapsulated complexes. These observations indicate that the framework of the zeolite has not undergone any significant structural change during encapsulation. This is expected as ligand being flexible in nature enters slowly through pores of the zeolite and fits nicely in the cavity upon coordination with the metal ions. Two new but week peaks due to neat complexes were detected in the encapsulated zeolite at 2θ values of 7.7 and 9.05 due to loading of metal complexes.

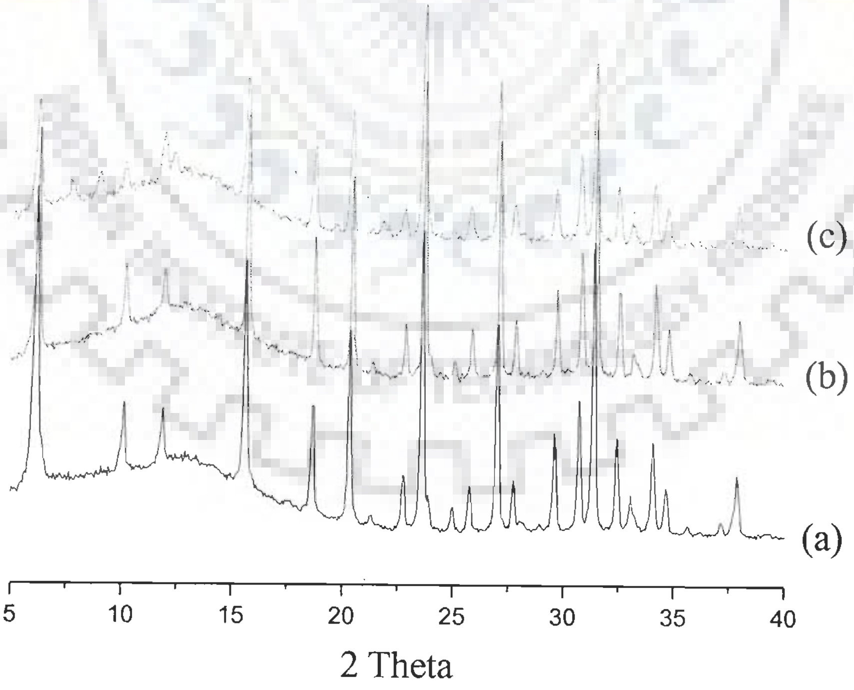


Figure 4.2. XRD pattern of (a) Na-Y, (b) Cu-Y and (c) [Cu(sal-oaba)(H_2O)]-Y.

4.3.4. Thermogravimetric analysis

The thermogravimetric analysis data along with the percent weight loss at different steps and their possible assignments are presented in Table 4.2. A representative TGA profile of [Cu(sal-oaba)(H_2O)]-Y is presented in Figure 4.3. The thermograms of catalysts, [VO(sal-oaba)(H_2O)]-Y (**4.1**) , [Cu(sal-oaba)(H_2O)]-Y (**4.2**) and [Ni(sal-oaba)(H_2O)$_3$]-Y (**4.3**) indicate their decomposition in three steps, though these steps are overlapping. The exothermic removal of just trapped water of ca. 4.2 % (in **4.1**), ca. 4.7 % (in **4.2**) or ca. 3.3 % (in **4.3**) occurs up to 150° C, while an endothermic weight loss of ca. 6.3 % (in **4.1**), ca. 8.0 % (in **4.2**) or ca. 6.1 % (in **4.3**) associated with removal of intrazeolite water occurs in the temperature range 150–350° C. As all encapsulated complexes have one or more water molecules coordinated, their removal in this step is also expected. The third step involves the slow but exothermic weight loss of ca. 13.1 % (in **4.1**), ca. 15.6 % (in **4.2**) or ca. 9.1 % (in **4.3**) in a wider temperature range due to decomposition of the metal complexes. A low weight loss percentage in higher temperature range is in agreement with the low percentage of metal content obtained for encapsulated complexes.

Table 4.2. Thermogravimetric analysis data of catalysts

Catalyst	Temp. range (°C)	Weight loss (%)	Group lost
[VO(sal-oaba)(H_2O)]-Y	70-150 150-350 350-800	4.2 6.3 13.1	H_2O nH_2O L
[Cu(sal-oaba)(H_2O)]-Y	70-150 150-350 350-800	4.7 8.0 15.6	H_2O nH_2O L
[Ni(sal-oaba)(H_2O)$_3$]-Y	70-150 150-350 350-800	3.3 6.1 9.1	H_2O nH_2O L

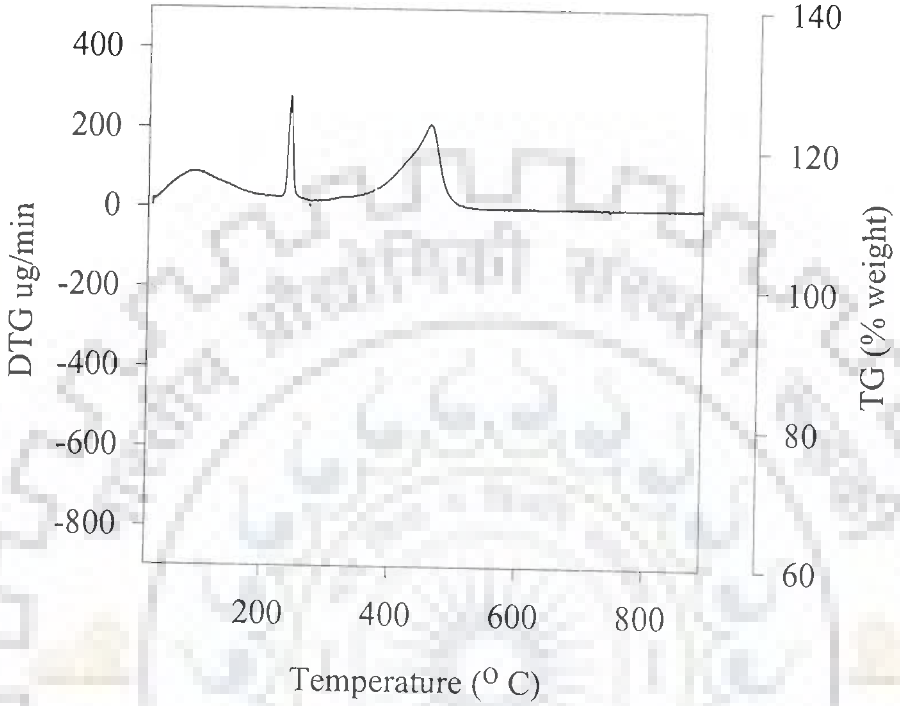


Figure 4.3. TG (dotted line) and DTG (solid line) profiles of [Cu(sal-oaba)]-Y.

4.3.5. Spectral studies

Table 4.3 lists IR and electronic spectral data of ligand and complexes. The intensity of the peaks in encapsulated complexes is, though, weak due to their low concentration in zeolite matrix, the spectra of encapsulated as well as their neat complexes showed essentially similar bands. Comparison of the spectra of these catalysts with the ligand provides evidence for the coordinating mode of ligand in catalysts.

The IR spectrum of ligand H_2sal-oaba exhibits a medium intensity band around 2700 cm^{-1} due to intra-molecular hydrogen bonding. Absence of this band in the spectra of encapsulated complexes indicates the destruction of the hydrogen bond followed by the coordination of phenolic and alcoholic oxygen after deprotonation.

The sharp band appearing at 1617 cm^{-1} due to the ν(C=N) (azomethine) shifts to lower wave number and appears at 1610–1615 cm^{-1}. This indicates the coordination of azomethine nitrogen to the metal ions. Neat complex [VO(sal-oaba)] exhibit a sharp band at 985 cm^{-1} due to the ν(V=O) stretch [166], while in zeolite encapsulated vanadium complex location of band due to V=O structure has not been possible due to the appearance of a strong and broad band at ca. 1000 cm^{-1}due to zeolite frame work.

Table 4.3. IR and electronic spectral data of ligand, pure and encapsulated complexes

Compound	IR (cm^{-1})	λ_{max} (nm)
H_2sal-oaba	1617, 1565, 1482, 1455, 1179, 1032	212, 228, 269, 338
[VO(sal-oaba)(H_2O)]-Y	1637, 1612, 1584, 1450,	221,263,404
[Cu(sal-oaba)(H_2O)]-Y	1645, 1615,1585, 1437, 787	222, 240, 291, 402
[Ni(sal-oaba)(H_2O)$_3$]-Y	1646, 1612, 1441, 784,	217, 264, 401
[VO(sal-oaba)]	1610, 1580, 1464, 1441, 1152, 985	272, 307,398, 525
[Cu(sal-oaba)]	1612, 1579, 1441, 1027, 752, 642	208,262,295,405, 600
[Ni(sal-oaba)(H_2O)$_3$]	1612, 1580, 1112, 759, 652	209,233,296,404

Electronic spectral studies of H_2sal-oaba and its complexes, [VO(sal-oaba)], [Cu(sal-oaba)] and [Ni(sal-oaba).3H_2O] have been studied in detail by Syamal *et al.* [166-168]. Their spectral data also presented in Table 4.3 are similar to those reported. As they have recorded diffused reflectance spectra of complexes, a partial difference in their positions has been noted in ligand bands. Similarly, we have observed only one d – d band for complexes [VO(sal-oaba)] and [Cu(sal-oaba)] at 525 and 600 nm, respectively. No such d – d band(s) could be observed for [Ni(sal-oaba)(H_2O)$_3$]. Electronic spectra of encapsulated complexes recorded in nujol exhibit essentially similar spectral features but their intensities are relatively poor. The expected d – d bands in these complexes could not be located possibly due to their poor loading. Figure 4.4 reproduces the electronic spectra of these encapsulated complexes.

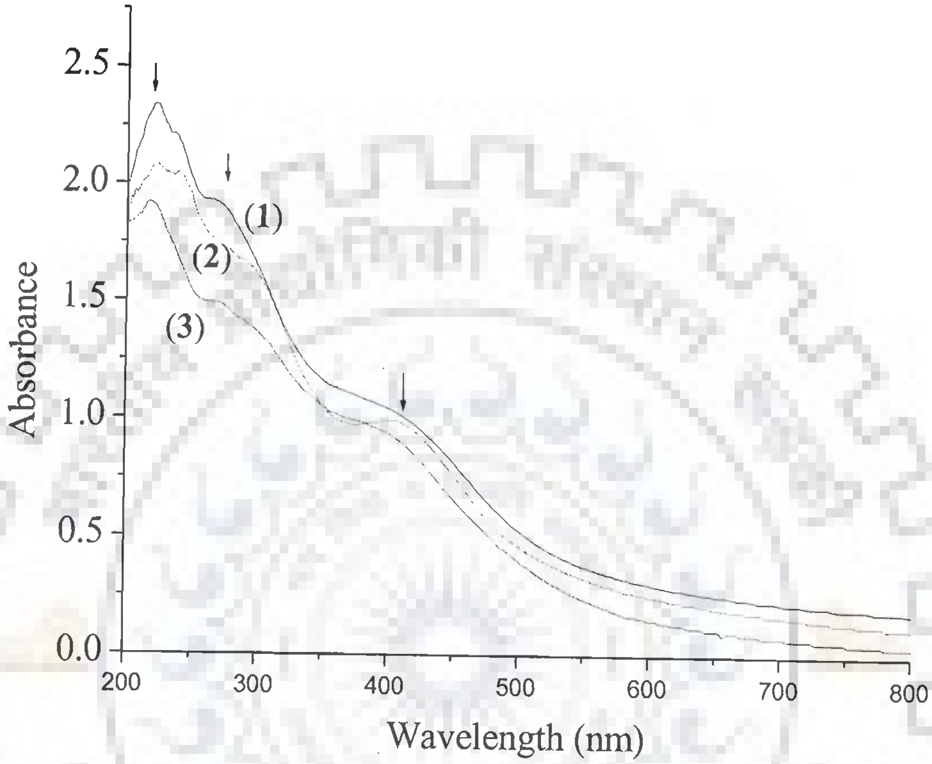
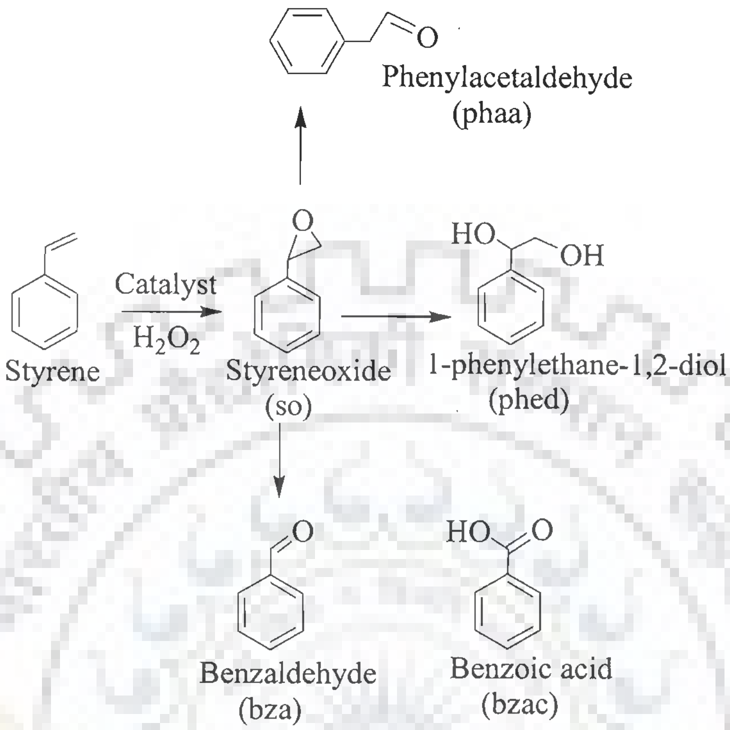


Figure 4.4. Electronic spectra of [VO(sal-oaba)(H_2O)]-Y (1), [Cu(sal-oaba)(H_2O)]-Y (2) and [Ni(sal-oaba)(H_2O)$_3$]-Y (3).

4.3.6. Catalytic activity studies

4.3.6.1. Oxidation of styrene

Oxidation of styrene, catalysed by [VO(sal-oaba)(H_2O)]-Y, [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)(H_2O)$_3$]- Y, using H_2O_2 as an oxidant gave styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde; Scheme 4.2. Some of these products have also been identified by others [128, 153, and 142]. Recently, the formation of all these products have been observed when polymer-supported catalyst, PS-[VO(sal-ohyba)(DMF)] (H_2sal-ohyba = Schiff base derived from salicylaldehyde and *o*-hydroxybenzylalcohol) having an isomeric ligand of H_2sal-oaba was applied [6].



Scheme 4.2

Reaction conditions have been optimised considering [VO(sal-oaba)(H_2O)]-Y as a representative catalyst and varying different reaction parameters viz. amount of catalyst and oxidant, and temperature of the reaction mixture to achieve maximum oxidation of styrene. Amount of H_2O_2 has considerable effect on the oxidation of styrene as has been demonstrated during the experiments considering four different styrene to H_2O_2 molar ratios at the fixed amount of styrene (1.04 g, 10 mmol), catalyst (0.025 g), CH_3CN (20 ml) and temperature (80 °C). As shown in Figure 4.5, the conversion of styrene improved from 44.2 to 56.1 % on increasing the styrene to H_2O_2 molar ratio from 1:1 to 1:1.5. This conversion further improved to 88.7 % at 1:2 (styrene to H_2O_2) molar ratio and finally a decreasing trend was observed at 1:2.5 ratio. The reason for the decreasing trend may be due to dilution of the reaction mixture by the presence of larger amount of water molecules in H_2O_2 solution. Thus, it is clear that the 1:2 molar ratio is the best one to obtain the optimum styrene conversion of 88.7 % in 6 h reaction time.

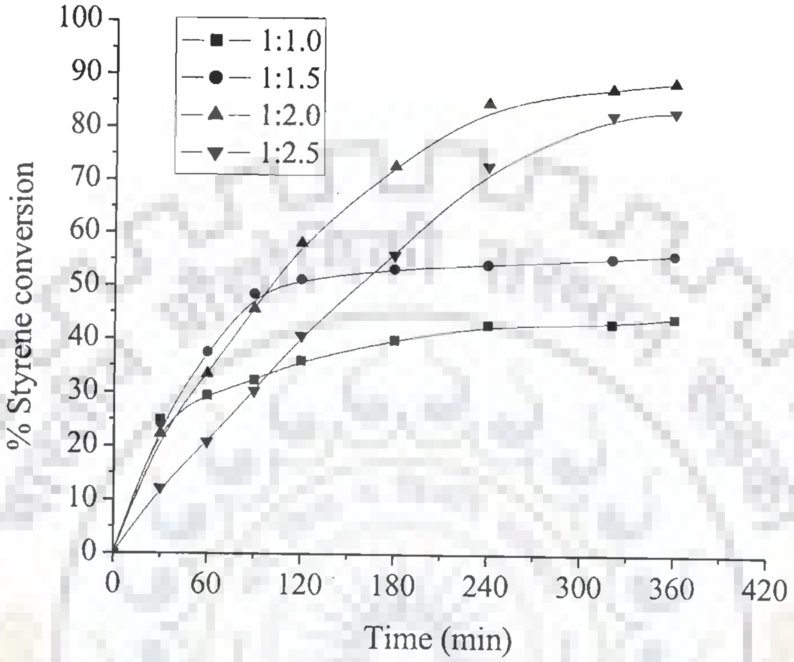


Figure 4.5. Effect of amount of oxidant on the oxidation of styrene.

Similarly, four different amounts of catalyst viz. 0.015, 0.025, 0.035 and 0.05 g were considered while keeping the fixed amounts of styrene (1.04 g, 10 mmol), aqueous H_2O_2 (2.28 g, 20 mmol) and CH_3CN (20 ml), and reaction was carried out at 80 °C. Figure 4.6 presents the results of percent styrene conversion as a function of time. It is seen from the figure that 0.015 g catalyst gave only 51.2 % conversion, while 0.025 g catalyst has shown a maximum conversion of 88.7 %. Further increment of catalyst amount to 0.035 g marginally improves this conversion while a decreasing trend has been observed with 0.050 g catalyst. Thus, at the expense of H_2O_2, 0.025 g catalyst may be considered sufficient enough to carry out the reaction with good conversion. The reason for reduced activity at higher catalyst dose may possibly be attributed to adsorption/ chemisorption of two reactants on separate catalyst particles, thereby reducing the chance to interact.

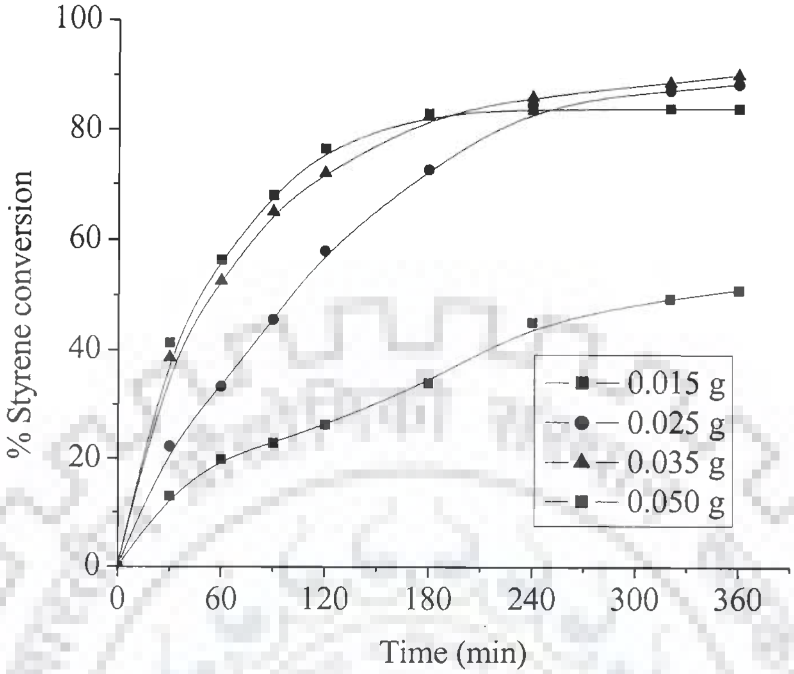


Figure 4.6. Effect of amount of catalyst on the oxidation of styrene.

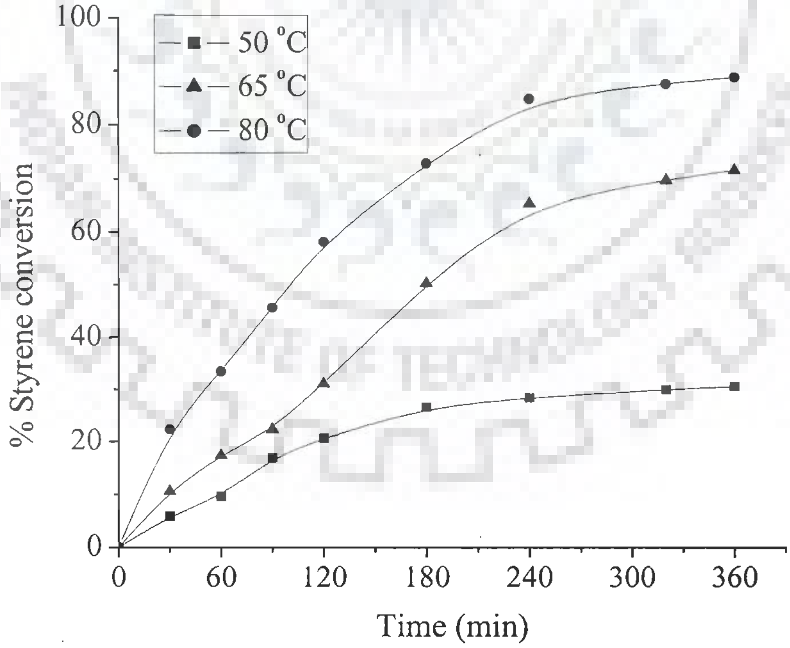


Figure 4.7. Effect of temperature on the oxidation of styrene.

Figure 4.7 illustrates the effect of temperature on the oxidation of styrene at the above optimised conditions. Amongst three different temperatures (50, 65 and 80 °C) studied, catalytic reaction at 80 °C had maximum oxidation of styrene. Also, the reaction reaches to its equilibrium in less time at this temperature.

Thus, for the maximum oxidation of 10 mmol of styrene other required parameters as concluded are: [VO (sal-oaba)(H_2O)]-Y (0.025 g), H_2O_2 (2.28 g, 20 mmol), CH_3CN (20 ml) and temperature (80 °C). After acquiring the optimised reaction conditions for [VO(sal-oaba)(H_2O)]-Y with H_2O_2 as oxidant, other catalysts e.g. [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)(H_2O)$_3$]-Y were also tested under identical conditions i.e. 10 mmol styrene, 20 mmol 30 % H_2O_2, 0.025 g catalyst and 20 ml CH_3CN at 80 °C for the oxidation of styrene. The results presented in Figure 4.8 show that the percentage conversion follow the order: [VO(sal-oaba)(H_2O)]-Y (88.7) % > [Cu(sal-oaba)]-Y (23.4) % > [Ni(sal-oaba) (H_2O)$_3$]-Y (6.6) %. Catalytic activites of neat complexes have also been tested using same mole concentration of complex as taken in case of encapsulated complexes and the reaction performed under similar conditions as mentioned above. As shown in Figure 4.9, these complexes have shown very poor catalytic activity. However, they also maintain the same order of catalytic efficiency for various products. Thus, the catalytic activity of the encapsulated complexes is better than their respective neat analogues.

Tert-butylhydroperoxide was also used as oxidant for the oxidation of styrene. The oxidation of styrene at the styrene / TBHP molar ratio of 1:2 at fixed amount of styrene (1.04 g, 10 mmol), CH_3CN (20 ml) and reaction temperature (80 °C) gave a maximum of 19.7 % conversion while higher as well as lower molar ratios gave lower conversions. The catalytic activities of other catalysts using TBHP as oxidant under the above conditions have been carried out and results are presented in Figure 4.10. It is clear from the figure that [Cu(sal-oaba)(H_2O)]-Y has a maximum of 30.2 % conversion which is followed by [VO(sal-oaba)(H_2O)]-Y with 19.7 % and [Ni(sal-oaba)(H_2O)$_3$]-Y showing only 10.3 % conversion. Under similar conditions, neat complexes were also tested and as shown in Figure 4.10, they have poorer performance.

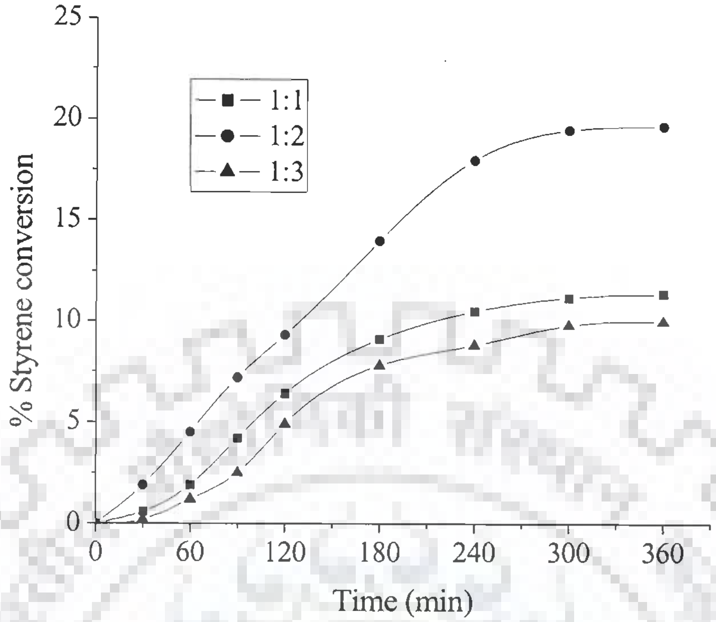


Figure 4.8. Effect of TBHP concentration (TBHP : styrene ratio) on the oxidation of styrene.

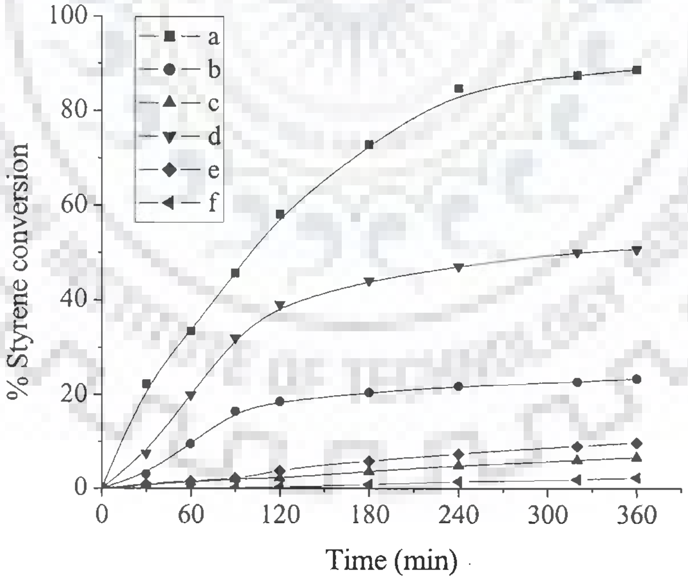


Figure 4.9. Catalytic activity of [VO(sal-oaba)(H_2O)]-Y (a), [Cu(sal-oaba)(H_2O)]-Y (b), [Ni(sal-oaba)(H_2O)$_3$]-Y (c), [VO(sal-oaba)] (d), [Cu(sal-oaba)] (e) and [Ni(sal-oaba)(H_2O)$_3$]-Y (f) for the oxidation of styrene using H_2O_2 as oxidant.

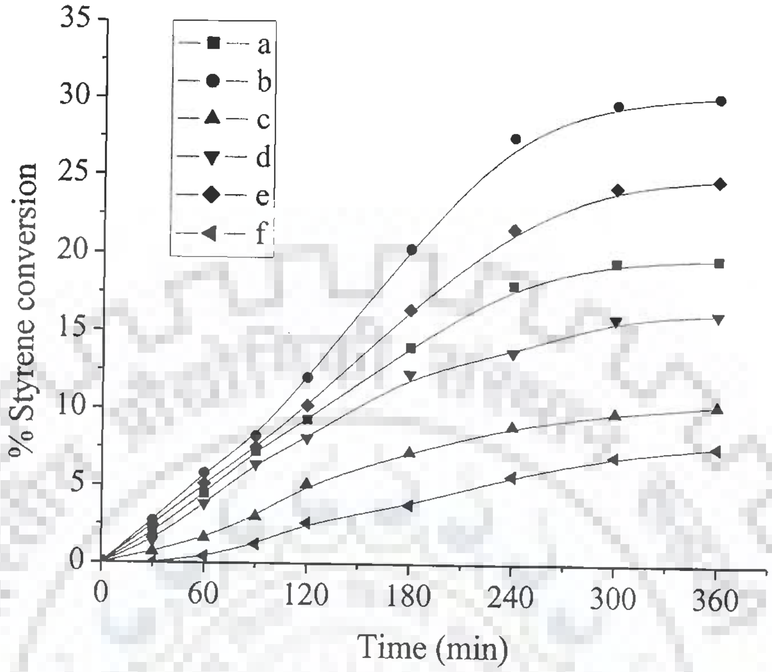


Figure 4.10. Effect of catalysts [VO(sal-oaba)(H_2O)]-Y (a), [Cu(sal-oaba)(H_2O)]-Y (b), [Ni(sal-oaba) (H_2O)$_3$]-Y (c), [VO(sal-oaba)] (d), [Cu(sal-oaba)] (e) and [Ni(sal-oaba)(H_2O)$_3$]-Y (f) on the oxidation of styrene using TBHP as oxidant.

Table 4.4.

Products selectivity and percent conversion of styrene after 6 h of reaction time using H_2O_2 as oxidant

Catalyst	% conv.	TOF[a] (h^{-1})	% Product selectivity[b]					
			so	bza	phed	bzac	phaa	Other
[VO(sal-oaba)(H_2O)]-Y	88.7	696.0	6.8	58.8	24.1	6.7	2.1	1.5
[Cu(sal-oaba) (H_2O)]-Y	23.4	180.1	15.8	68.2	0	9.1	5.7	1.2
[Ni(sal-oaba)(H_2O)$_3$]-Y	6.6	103.3	0	98.4	0	0	0	1.6
[VO(sal-oaba)]	50.7	397.8	6.9	74.2	8.9	4.1	4.9	1.0
[Cu(sal-oaba)]	9.5	73.1	9.7	77.4	0	9.6	2.2	1.1
[Ni(sal-oaba)(H_2O)$_3$]-Y	2.3	36.0	0	98.8	0	0	0	1.2

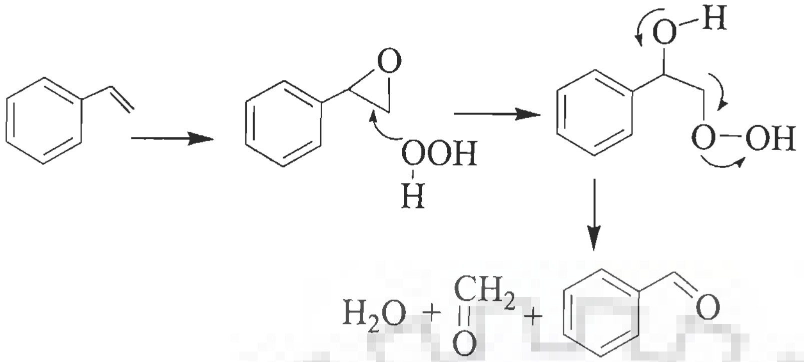
[a] TOF h^{-1} (Turnover frequency): moles of substrate converted per mole of metal (in the solid state catalyst) per hour

[b] For abbreviations see Scheme 4.2

Table 4.5. Products selectivity and percent conversion of styrene with TBHP after 6 h of reaction time

Catalyst	% Conv.	TOF (h^{-1})	% Product selectivity					
			so	bza	phed	bzac	phaa	Other
[VO(sal-oaba)(H_2O)]-Y	19.7	154.6	60.4	31.3	3.9	1.5	0	2.9
[Cu(sal-oaba) (H_2O)]-Y	30.2	232.4	71.0	21.3	2.0	0	1.4	4.3
[Ni(sal-oaba)(H_2O)$_3$]-Y	10.3	161.2	43.4	49.2	0	0	0	7.4
[VO(sal-oaba)]	16.2	127.1	57.4	31.7	4.3	0	0.8	0.9
[Cu(sal-oaba)]	24.8	190.9	60.9	20.5	8.5	0	2.6	7.5
[Ni(sal-oaba)(H_2O)$_3$]	7.6	118.9	39.6	52.5	0	0	0	7.9

Table 4.4 analyses the selectivity of various products using H_2O_2 as oxidant, while Table 4.5 gives details using TBHP as oxidant. In case of [VO(sal-oaba)(H_2O)]-Y, the selectivity of various reaction products follow the order: benzaldehyde >1-phenylethane-1,2-diol > benzoic acid > styrene oxide > phenylacetaldehyde, while for [Cu(sal-oaba)(H_2O)]-Y catalyst, the order is: benzaldehyde > styrene oxide > phenyl acetaldehyde > benzoic acid. As high as 15.8 % selectivity of an important reaction product styrene oxide has only been obtained with [Cu(sal-oaba)(H_2O)]-Y while other catalysts have shown very poor selectivity towards styrene oxide. Catalyst, [Ni(sal-oaba)(H_2O)$_3$]-Y was highly selective towards the formation of benzaldehyde and gave only small amount of other products. A highest yield of benzaldehyde is possibly due to further oxidation of styrene oxide formed in the first step by a nucleophilic attack of H_2O_2 on styrene oxide followed by cleavage of the intermediate hydroperoxistyrene; Scheme 4.3. Oxidative cleavage of the styrene side chain double bond via a radical mechanism may also produce benzaldehyde. High amount of water present in H_2O_2 is partly responsible for the possible hydrolysis of styrene oxide to 1-phenylethane-1,2-diol. Other products in limited percentage e.g. benzoic acid may form through further oxidation of benzaldehyde. Similarly, the formation of phenylacetaldehyde may occur through isomerisation of styrene oxide.



Scheme 4.3

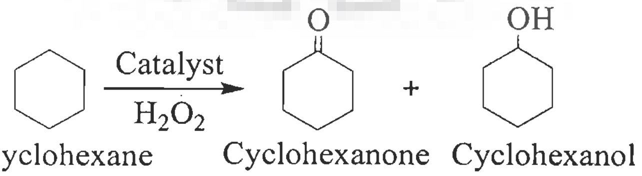
Using TBHP, a milder oxidant, the reaction is highly selective towards the formation of styrene oxide with all neat as well as encapsulated complexes. Its selectivity order for encapsulated complex is: [Cu(sal-oaba)(H_2O)]-Y (71.0 %) > [VO(sal-oaba)(H_2O)]-Y (60.4 %) > [Ni(sal-oaba)(H_2O)$_3$]-Y (43.4 %). This is followed by the formation of benzaldehyde. The selectivity of other two or three reaction products has no definite trend. Table 4.5 summarises the results along with the turn over frequency for conversion of styrene after 6 h of reaction time using TBHP as oxidant.

Catalytic potential of these complexes compare well with similar encapsulated complexes. About 34.8% conversion of styrene was noted with zeolite-Y encapsulated [VO(salphen)] (H_2salphen = Schiff base derived from salicylaldehyde and *o*-phenylenediamine) using 70 % tert-butylhydroperoxide as an oxidant [128]. Zeolite-Y encapsulated catalyst [VO_2(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y (Hsal-ambmz = Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole) exhibits ca. 97 % and 56.7 % conversion of styrene, respectively, using H_2O_2 as oxidant. Catalyst [Mn(salen)]-Y (H_2salen = Schiff base derived from salicylaldehyde and ethane-1,2-diamine) exhibits ca. 30 % conversion of styrene using molecular oxygen as an oxidant in excess of *tert*-butylhydroperoxide as initiator [153]. The observed conversions for zeolite-Y encapsulated complexes [Mn(Cl_2-haacac)Cl]-NaY (89.7%) [36], [Mn((NO_2)$_2$-haacac)Cl]-NaY (96.9%)

(H_2haacac = bis(2-hydroxyanil)acetylacetone) [169] with *tert*-butylhydroperoxide as initiator and air as oxidant are close to the one reported in Table 4.5. Zeolite encapsulated catalysts [Mn(3-MeOsalen)]-Y (H_2salen = bis(salicylaldehyde)-1,2-diaminoethane), [Mn(3-MeOsalpn)]-Y and [Mn(salpn)]-Y (H_2salpd = bis(salicylaldehyde)-1,3-diaminopropane) exhibit 17 %, 8.7 % and 7.4 % conversions, respectively, using *tert*-butylhydroperoxide as oxidant [76]. About 80 % conversion of styrene was observed with polymer-supported catalyst PS-K[VO_2(sal-ohyba)]. The selectivity of styrene oxide with all these catalysts is always low [6].

4.3.6.2. Oxidation of cyclohexane

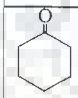
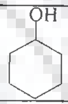
The activity tests of the prepared catalysts were also carried out for the oxidation of cyclohexane. After several trials, the best suited reaction conditions for the oxidation of 10 mmol of cyclohexane were concluded as follows: catalyst (0.040 g), CH_3CN (20 ml) and reaction temperature (70 °C). Under the optimized reaction conditions, the encapsulated complexes, [VO(sal-oaba)(H_2O)]-Y and [Cu(sal-oaba)(H_2O)]-Y were tested for the oxidation of cyclohexane and the results obtained after 2 h of reaction time are summarized in Table 4.6. A maximum of 45.8 % conversion has been achieved with [Cu(sal-oaba)(H_2O)]-Y, while [VO(sal-oaba)(H_2O)]-Y gave only 21.0 % conversion with major products of cyclohexenol and cyclohexanone as shown in Scheme 4.4. The selectivity of these products varies in the order: cyclohexanone > cyclohexanol. A small amount (ca. 5 %) of an unidentified product has also been observed and is possibly cyclohexane-1,2-diol. The formation of cyclohexane-1,2-diol has recently been identified when [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y were used as catalyst [see previous chapter].



Scheme 4.4

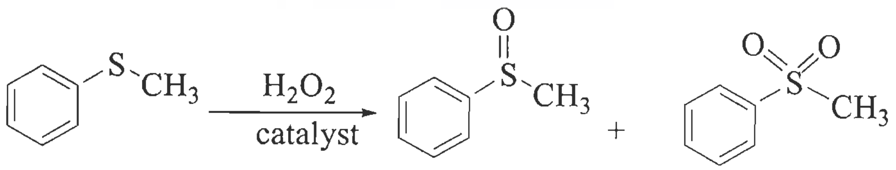
Same mole concentrations of neat complexes, as used for encapsulated ones, have shown poor convertion under above mentioned reaction conditions (see Table 4.6). However, the selectivity of cyclohexenol is better than cyclohexanone. The turn over frequencies for these complexes are also relatively less than that of the encapsulated ones.

Table 4.6. Effect of different catalysts on the oxidation of cyclohexane and product selectivity

Catalyst	% conv.	TOF (h^{-1})	% Product selectivity		
					Other
[Cu(sal-oaba)(H_2O)]-Y	45.8	220.3	50.7	44.8	4.5
[VO(sal-oaba)(H_2O)]-Y	14.8	72.6	56.7	38.5	4.8
[Cu(sal-oaba)]	11.4	54.8	42.2	51.3	6.5
[VO(sal-oaba)]	4.7	23.1	40.4	57.4	2.2

4.3.6.3. Oxidation of methyl phenyl sulfide (thioanisol)

The sulfur atom of the methyl phenyl sulfide is electron rich and has been shown to undergo electrophilic oxidation to give sulfoxide. Such oxidation of methyl phenyl sulfide by aqueous 30 % H_2O_2 has been carried out using [VO(sal-oaba)(H_2O)]-Y , [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)(H_2O)$_3$]-Y as catalysts. Two oxidation products as shown by Scheme 4.5 have been obtained.



Scheme 4.5

In order to get optimum reaction conditions, amount of oxidant and catalyst were varied while carrying out the reaction at room temperature. The effect of H_2O_2 concentration on the oxidation of methyl phenyl sulfide is illustrated in Figure 4.11. Three different methyl phenyl sulfide / aqueous 30 % H_2O_2 molar ratios viz. 1:0.5, 1:1 and 1:2 were considered at the fixed amounts of methyl phenyl sulfide (0.62 g, 5 mmol) and catalyst [VO(sal-oaba)(H_2O)]-Y (0.015 g) in 20 ml of CH_3CN. Increasing the ratio from 1:0.5 to 1:1 increased the conversion from 42.5 % to 93.2 % in 3 h of reaction time. On further increasing the ratio to 1: 2, though marginally improved this conversion, this molar ratio influenced to reduce the completion of the reaction time considerably. However, at the expense of H_2O_2, methyl phenyl sulfide / aqueous 30 % H_2O_2 molar ratio of 1:1 has been considered the most appropriate to proceed.

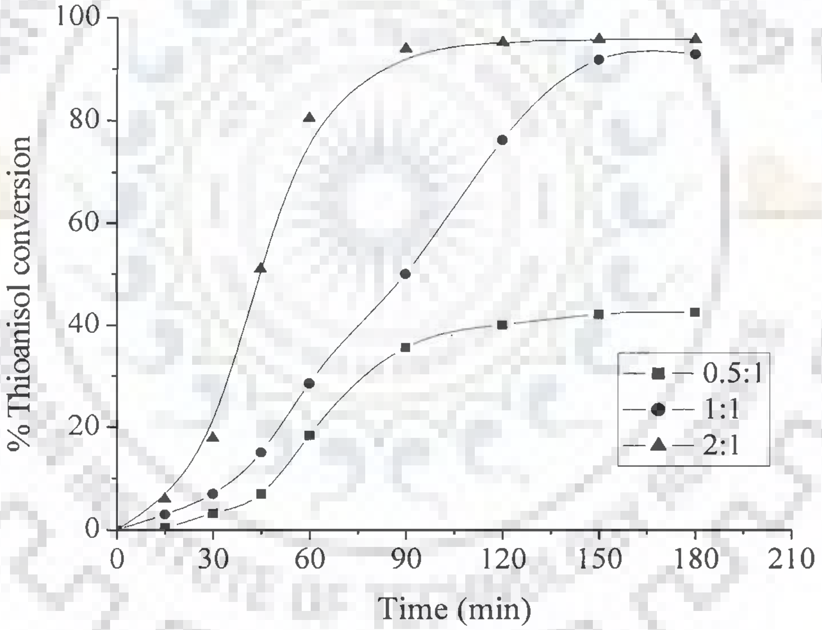


Figure 4.11. Effect of H_2O_2: thioanisol molar ratio on the oxidation of thioanisol.

Similarly, four different amounts of catalyst (viz. 0.005, 0.015, 0.025 and 0.035 g) were considered for 5 mmol of methyl phenyl sulfide under above mentioned reaction conditions and the results obtained are presented in Figure 4.12 as function of reaction time. It is clear from the figure that 0.015 g catalyst is sufficient enough to give 93.2 % conversion in 3 h of reaction time. Higher amounts of catalyst influence only to reduce the equilibrium time of the reaction. The selectivity percentages of methyl phenyl sulfoxide and methyl phenyl sulfone at the methyl phenyl sulfide : aqueous 30 % H_2O_2 molar ratio of 1:1 are 96.9 % and 3.1 %, respectively.

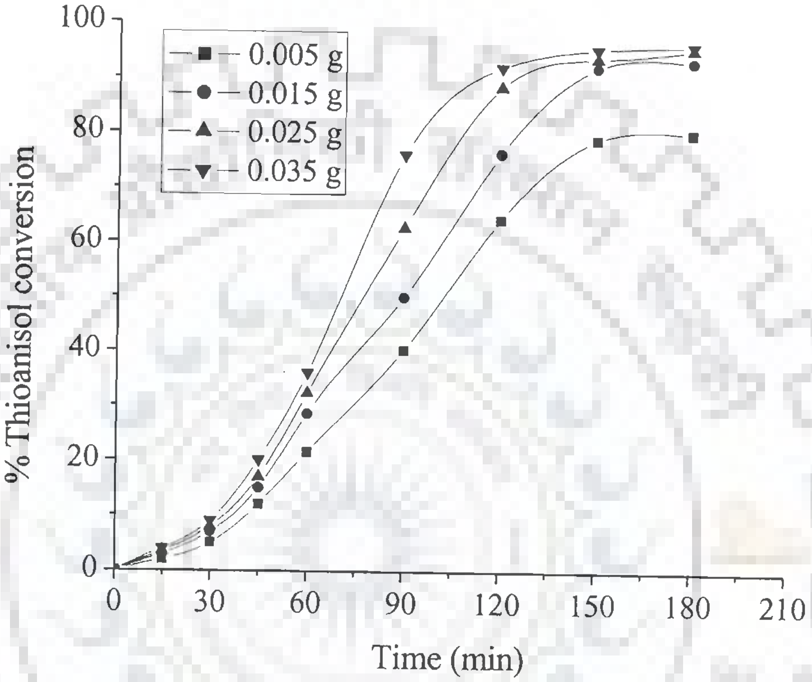


Figure 4.12. Effect of amount of catalyst on the oxidation of thioanisol.

A blank reaction under similar conditions i.e. methyl phenyl sulfide (5 mmol), aqueous 30 % H_2O_2 (5 mmol) and CH_3CN (20 ml), resulted in 37.5 % conversion where 69.3 % selectivity was registered for sulfoxide and 30.7 % for sulfone. Thus, the complex [VO(sal-oaba)(H_2O)]-Y not only enhanced the percent conversion of methyl phenyl sulfide, it also improved the selectivity for sulfoxide. The catalytic performances of these encapsulated complexes compare well with the data recently reported for zeolite-Y encapsulated [VO_2(sal-ambmz)]-Y which exhibits 97 % conversion.

After acquiring the optimised reaction conditions for [VO(sal-oaba)(H_2O)]-Y, other catalysts e.g. [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)$(H_2O)_3$]-Y were also tested. Unfortunately these catalysts did not show appreciable effect on the conversion of methyl phenyl sulfide and thus, they seem to be catalytically inactive for sulfide oxidation.

Neat complexes, [VO(sal-oaba)], [Cu(sal-oaba)] and [Ni(sal-oaba)(H_2O)$_3$] were also tested for catalytic activity using same mole concentration as zeolite encapsulated one under above mentioned optimised conditions. Again, [Cu(sal-oaba)] and [Ni(sal-oaba)(H_2O)$_3$] did not show any catalytic activity, while [VO(sal-oaba)] has shown a maximum of 91.4 % conversion showing the catalytic activity comparable to that of encapsulated vanadium complex. The selectivity of the products is also comparable. Table 4.7 summarises products selectivity and conversion details for vanadium complexes.

Table 4.7. Percent conversion of thioanisol and selectivity of sulfoxide and sulfone formation at room temperature after 3 h of contact time

Catalyst	% Conv.	TOF (h^{-1})	% Selectivity	
			Methyl phenyl sulfoxide	Methyl phenyl sulfone
[VO(sal-oaba)(H_2O)]-Y	93.2	597.8	96.9	3.1
[VO(sal-oaba)]	91.4	586.2	98.4	1.6
Without catalyst	37.5	-	69.3	30.7

4.3.7. Possible reaction pathway of the catalysts

We have tried to establish the possible reaction pathway of the catalysts during catalytic action by reacting methanolic solution of neat complexes [VO(sal-oaba)] and [Cu(sal-oaba)] with H_2O_2 dissolved in methanol and monitoring the changes by electronic absorption spectroscopy. Thus, the treatment of ca. 10^{-4} M solution of [VO(sal-oaba)] in methanol with one drop portions of 30 % H_2O_2 dissolved in minimum amount of methanol caused the slow disappearance of 307 and 398 nm bands while the intensity of 350 nm bands slowly increased with slight shift at 330 nm. The band appearing at 272 nm mainly gained intensity; Figure 4.13. The weak broad d – d band at 525 nm slowly disappeared (see inset Figure 4.13). Similarly, titration of [Cu(sal-oaba)] with H_2O_2 resulted in the partial decrease in the intensities of 405 (see inset of Figure 4.14) and 600 nm bands while partial increase in the intensity of 296 nm band with broadening; Figure 4.14. The band appearing at 262 nm gained intensity. All these suggest the formation of peroxo species on the interaction of [VO(sal-oaba)] and [Cu(sal-oaba)] with H_2O_2. The in situ generation of peroxo species has been observed previously by oxovanadium(IV) and copper(II) complexes by interaction of such complexes with oxidants like H_2O_2 and tert-butylhydroperoxide. This in situ generated peroxo species finally transfer oxygen to the substrates to give oxidized products. Thus, the reversible intermediate formation of facile peroxo species may be responsible for the catalytic performance of the encapsulated species. This is further supported by the fact that isolation of peroxovanadium(V) complex of H_2sal-oaba by reacting [VO(sal-oaba)] with H_2O_2 always failed and ended up with the starting complex [VO(sal-oaba)].

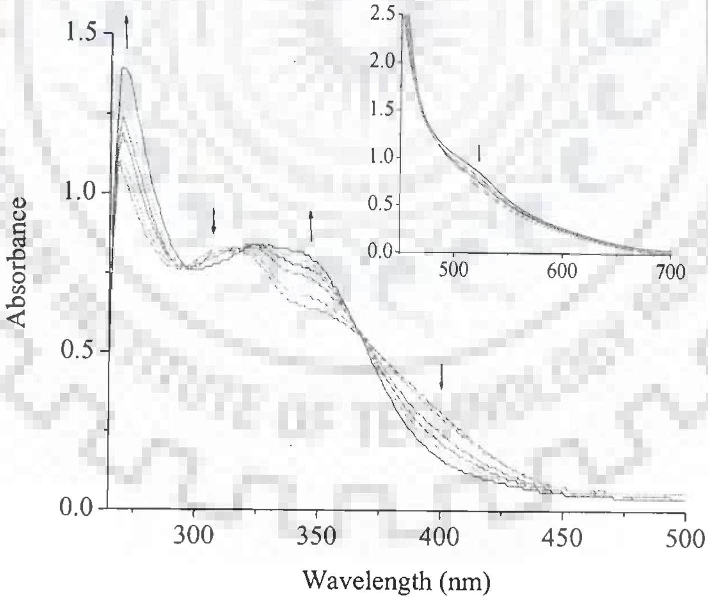


Figure 4.13. Titration of [VO(sal-oaba)] with H_2O_2. The spectra were recorded after successive addition of one drop portions of H_2O_2 in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of [VO(sal-oaba)] in methanol. The plots presented in inset were recorded in DMSO.

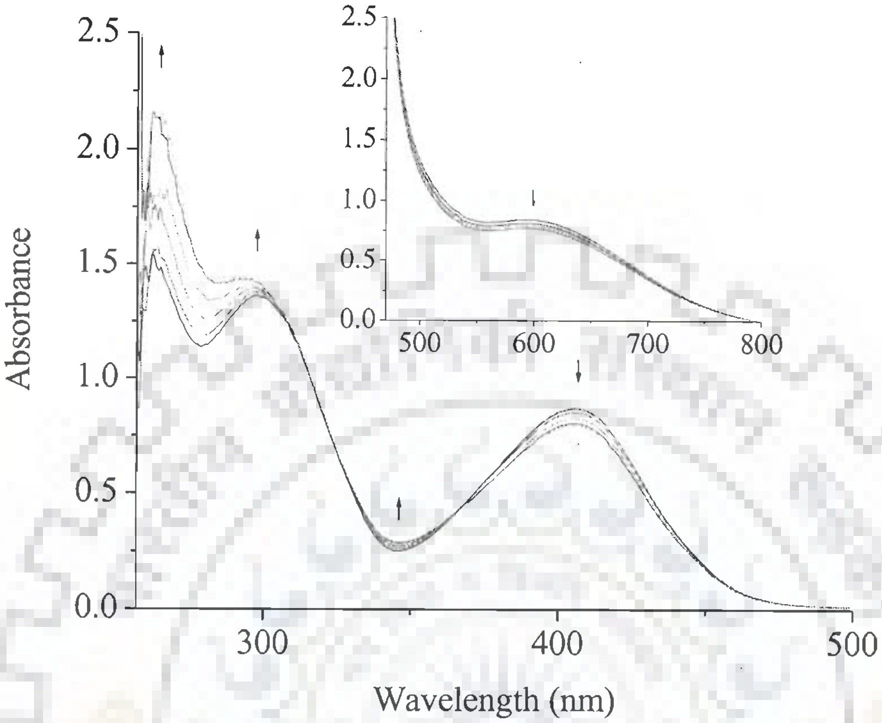


Figure 4.14. Titration of [Cu(sal-oaba)] with H_2O_2. The spectra were recorded after successive addition of one drop portions of H_2O_2 in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of [Cu(sal-oaba)] in methanol. The plots presented in inset were recorded in DMSO.

4.4. CONCLUSIONS

The zeolite encapsulated metal complexes, [VO(sal-oaba)(H_2O)]-Y, [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)(H_2O)$_3$]-Y have been prepared and characterised. Catalytic activities of these complexes have been tested for the oxidation of styrene, cyclohaxene and methyl phenyl sulfide using H_2O_2 as oxidant. Styrene catalysed by [VO(sal-oaba)(H_2O)]-Y gives five reaction products, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde. Except, 1-phenylethane-1,2-diol, all four products have also been obtained with [Cu(sal-oaba)(H_2O)]-Y. Styrene oxide, an important product has been obtained only in poor yield, while the yield of benzaldehyde is highest. Complex, [Ni(sal-oaba)$(H_2O)_3$]-Y gave benzaldehyde selectively, though conversion is only 6.6 %. With 45.8 % conversion of cyclohexane by [Cu(sal-oaba)(H_2O)]-Y, the selectivity of two products follow the order: cyclohexanone (50. 7 %)> cyclohexanol (44.8 %). [VO(sal-oaba)(H_2O)]-Y has shown only 14.8 % conversion. No oxidation of substrates has been observed in absence of catalysts. A maximum of 93.2 % conversion of methyl phenyl sulfide has been achieved with [VO(sal-oaba)(H_2O)]-Y using H_2O_2 as oxidant, where selectivity of sulfoxide and sulfone are 96.9 % and 3.1 %, respectively. Other catalysts are found inactive towards the oxidation of methyl phenyl sulfide. Neat complex, [VO(sal-oaba)] has shown equally good catalytic activity. All heterogeneous catalysts are stable and free from leaching as have been confirmed by testing the filtrate for the corresponding metal ion. They are recyclable at least up to two cycles.

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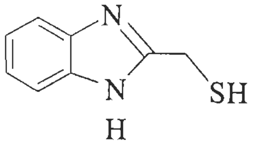
CHAPTER-5

Oxidation of methyl phenyl sulfide, diphenyl sulfide and styrene by oxovanadium(IV) and copper(II) complexes of NS donor ligand encapsulated in zeolite-Y

5.1. INTRODUCTION

Oxidation of sulfides (thioethers) to sulfoxides i.e. sulfoxidases activity, exhibited by enzymes vanadependent-dependent haloperoxidases, has been considered as one of the important catalytic reactions [145, 146, 170]. Several vanadium and molybdenum complexes model this reaction [171, 172]. Vanadium complexes also present functional model of haloperoxidases where these complexes catalyze the oxidative halogenation of aromatic substrates using H_2O_2 as oxidant in the presence of halides [173-175]. They have also been shown to be active homogeneous catalysts for other oxidation reactions [53, 176]. Oxovanadium(IV) complexes encapsulated in the cavity of zeolite-Y have also been reported and studied for the oxidation reactions. For example oxovanadium(IV) complexes of H_2salen based ligands encapsulated in zeolite-Y have shown good catalytic activity for the oxidation of phenol [59, 63, 64]. Complex, [VO(pic)$_2$] encapsulated in zeolite-Y has been studied for the oxidation of cyclohexene, n-hexane and toluene [177]. Leaching of the catalysts encapsulated in zeolite-Y has, however, been observed during catalytic action if the molecular size of the catalysts are too small [116]. Similarly copper(II) complexes encapsulated in the cavity of zeolite-Y exhibit several oxidation reactions.[17, 34, 68].

In this chapter, encapsulation of oxovanadium(IV) and copper(II) complexes of 2-mercaptomethylbzimidazole (Htbmz, **5.I**; Scheme 5.1), their characterization and catalytic activities for the oxidation of styrene, methyl phenyl sulfide and diphenyl sulfide are reported.



5.I: Htbmz

Scheme 5.1

5.2. EXPERIMENTAL

5.2.1. Materials and methods

Mercapto acetic acid (E. Merck, India), methyl phenyl sulfide (Alfa Aeaser, USA) and diphenyl sulfide (Himedia, India) were used as obtained. Y-zeolite (Si/Al ~ 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were of AR grade. Instrumentation and analyses details are reported in Chapter-2.

5.2.2. Preparations

5.2.2.1. Preparation of 2-mercaptomethylbenzimidazole (Htbmz, 5.I)

A mixture of *o*-phenylenediamine (10.8 g, 100 mmol) and merceptoacetic acid (9.1 g, 100 mmol) was dissolved in 4M HCl (150 ml) and the reaction mixture was refluxed for 3 days on a heating mantle. After keeping the flask at 10 °C overnight, the precipitated greenish crystals of Htbmz.HCl were filtered off and washed with acetone. On neutralization of Htbmz.HCl dissolved in minimum of water with K_2CO_3, yellow green solid of Htbmz separated out which was filtered, washed with minimum amount of cold water and dried in desiccator over NaOH. Yield: 11.1 g (68 %). M.p.: 157 °C (Lit. 157-158 °C) [178].

5.2.2.2. Preparation of M-Y (M = Cu(II) or OV(IV)

An amount of 5.0 g of Na-Y zeolite was suspended in 300 ml of distilled water and to this was added cupric nitrate (2.8 g, 12 mmol) for Cu(II)-Y or vanadyl sulfate (3.0 g, 12 mmol) for OV(IV)-Y with stirring at ca. 90 °C for 24 h. The light colour solid was filtered off, washed with hot distilled water until filtrate was free from any metal ion content and dried at ca. 120 °C for 24 h.

5.2.2.3. Preparation of $[VO^{IV}(tbmz)_2]$-Y (5.1) and $[Cu^{II}(tbmz)_2]$-Y (5.2): A general method

Encapsulated complexes were prepared using flexible ligand method. An amount of 1.0 g of Cu(II)-Y or OV(IV)-Y and 2.5 g ligand were mixed in 50 ml of methanol in a round bottom flask and the reaction mixture was heated under reflux for overnight in an oil bath while stirring. The resulting material was filtered, dried and soxhlet extracted with methanol followed by acetone to remove excess ligand and metal complex on the surface of zeolite. The uncomplexed metal ions in zeolite were removed by treating with aqueous 0.01M NaCl solution (200 ml) with stirring for 8 h. It was then washed with double distilled water till no precipitate of AgCl was observed in the filtrate on treating with $AgNO_3$. Finally they were dried at 120 °C till constant weight.

5.2.2.4. Preparation of $[VO^{IV}(tbmz)_2]$(5.3)

A solution of $VOSO_4.5H_2O$ (1.25 g, 5 mmol) in minimum amount of water was added drop wise to a methanolic solution of Htbmz (1.63 g, 10 mmol) and the obtained reaction mixture was refluxed on a water bath for 2 h. After keeping the flask at ambient temperature for over night, complex $[VO(tbmz)_2]$ slowly separated out, which was filtered, washed with methanol and dried in vacuum over silica gel.

5.2.2.5. Preparation of $[Cu^{II}(tbmz)_2]$(5.4)

A solution of $Cu(CH_3COO)_2 .H_2O$ (1.0 g, 5 mmol) dissolved in 50 ml of methanol was added to a methanolic solution of Htbmz (1.63, 10 mmol) with stirring. After addition of KOH (0.28 g, 5 mmol) dissolved in 5 ml of water with stirring, the reaction mixture was further stirred for 2 h. During this period $[VO(tbmz)_2]$ slowly separated out, which was filtered off, washed with minimum amount of methanol and dried in vacuum over silica gel.

5.2.3. Catalytic activity studies

5.2.3.1. Oxidation of styrene

The catalytic oxidation of styrene was carried out using complexes, $[VO(tbmz)_2]$-Y and $[Cu(tbmz)_2]$-Y in a 50 ml flask fitted with a water circulated condenser. In a typical reaction, an aqueous solution of 30 % H_2O_2 (2.28 g, 20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH_3CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The reaction was considered to begin after addition of 0.025 g of catalyst. During the reaction, the products were analyzed using a gas chromatograph by withdrawing small aliquots after specific interval of time and confirming their identities by GC-MS.

5.2.3.2. Oxidation of methyl phenyl sulfide and diphenyl sulfide

The catalytic oxidation of methyl phenyl sulfide and diphenyl sulfide was carried out using $[VO(tbmz)_2]$-Y in a 50 ml flask at room temperature. Methyl phenyl sulfide (0.62 g, 0.005 mol) or diphenyl sulfide (0.93 g, 5 mmol) and 30 % H_2O_2 (0.57 g, 5 mmol) was dissolved in 20 ml of acetonitrile. After addition of catalyst (0.015 g), the reaction mixture was stirred at room temperature for 3 h. During this period, the reaction products formed were analyzed using gas chromatograph by withdrawing small aliquots after specific interval of time. The identities of the products were confirmed by GC-MS.

5.3. RESULTS AND DISCUSSION

5.3.1. Characterization of catalysts

Synthesis of zeolite-Y encapsulated complexes represented as $[VO(tbmz)_2]$-Y (**5.1**) and $[Cu(tbmz)_2]$-Y(**5.2**) were completed in two steps. The first step involved the exchange of oxovanadium(IV) and copper(II) ions with Na^+ of Na-Y while second step involved the reaction of metal exchanged zeolite-Y with Htbmz (**5.I**) in methanol. Here, ligand entered into the cavity of zeolite-Y due to its flexible nature and interacted with metal ions. The crude mass was extracted with methanol and acetone to remove excess free ligand and neat metal complex formed on the surface of the zeolite, if any. The percentages of metal content determined before and after encapsulation by inductively coupled plasma along with their expected formula and color are presented in Table 5.1. As crude mass was extracted with methanol and acetone the metal ion content found after encapsulation is only due to the presence of metal complexes in the nano-cavity of the zeolite-Y. The molecular formula of the complexes are based on the neat complexes $[VO(tbmz)_2]$ and $[Cu(tbmz)_2]$ that have also been prepared by reacting the corresponding suitable metal precursor with the ligand and characterized.

Table 5.1. Chemical composition, physical and analytical data

No.	Catalyst	Colour	Metal content (wt %)
1	OV(IV)-Y	Light green	4.58
2	Cu(II)-Y	Pale blue-green	7.60
3	$[VO(tbmz)_2]$-Y, **5.1**	Light green	1.14
4	$[Cu(tbmz)_2]$-Y, **5.2**	Yellow green	2.58

5.3.2. Scanning electron micrograph studies

The scanning electron micrographs (SEM) of the metal exchanged zeolite and their respective encapsulated complexes indicate the presence of well defined crystals free from any shadow of the metal ions or complexes present on their external surface. The representative micrographs of (a) Cu(II)-Y and (b) $[Cu(tbmz)_2]$Y are presented in Figure 5.1.

5.3.3. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na-Y, OV(IV)-Y and Cu(II)-Y, and encapsulated metal complexes were recorded at 2θ values between 5 and 70°. The XRD patterns of Na-Y, Cu(II)-Y and $[Cu(tbmz)_2]$-Y are presented in Figure 5.2. An essentially similar pattern in Na-Y, metal ions exchanged zeolite and encapsulated metal complexes were noticed, though slight change in the intensity of the bands in encapsulated complexes is in line. These observations indicate that the framework of the zeolite has not undergone any significant structural change during incorporation of the catalysts i.e. crystallinity of the zeolite-Y is preserved during encapsulation. No new peaks due to neat complex were detected in the encapsulated zeolite possibly due to very low percentage loading of metal complexes.

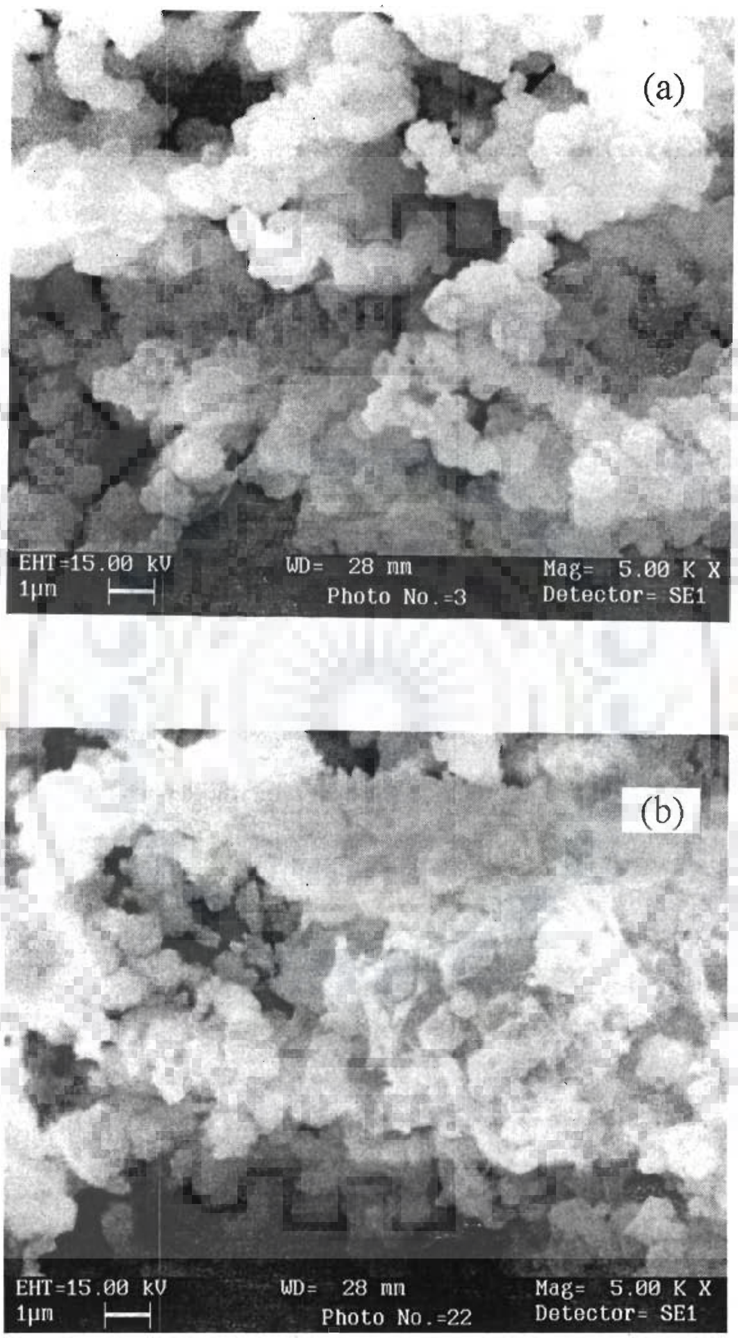


Figure 5.1. Scanning electron micrographs of (a) Cu-Y and (b) [Cu $(tbmz)_2$]-Y.

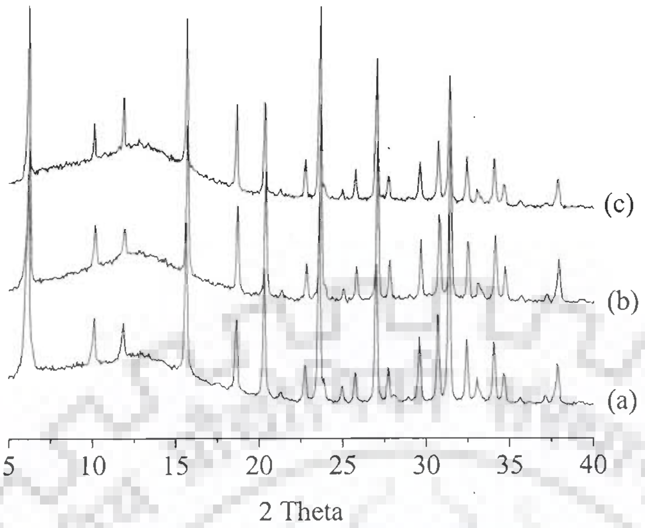


Figure 5.2. XRD patterns of (a) Na-Y, (b) Cu-Y and (c) [Cu(tbmz)$_2$]-Y

5.3.4. Thermogravimetric analysis

The thermogravimetric analysis data along with the percent weight loss at different steps and their possible assignments are presented in Table 5.2. TG and DTG profile of one representative complex [Cu(tbmz)$_2$]-Y is reproduced in Figure 5.3. The thermal decomposition of catalysts [VO(tbmz)$_2$]-Y (**5.1**) and [Cu(tbmz)$_2$]-Y (**5.2**) usually occurs in three steps. The removal of just trapped water of ca. 4.5 % (in **5.1**) or ca. 5.1 % (in **5.2**) occurs up to 150 °C, while an endothermic weight loss of ca. 5.8 % (in **5.1**) or ca. 5.2 % (in **5.2**) associated with removal of intrazeolite water occurs in the temperature range 150– 280 °C. The third step of exothermic weight loss consists of several sub steps and starts immediately after second step and continues till 800 °C to constant weight. A weight loss of ca. 13.0 % (in **5.1**) or ca. 13.4 % (in **5.2**) due to the slow decomposition of metal complexes is expected in this wide temperature range. The loss in percentage is in agreement with the percentage of metal content obtained for encapsulated complexes.

Table 5.2. Thermogravimetric analysis data of catalysts

Catalyst	Temp. range (°C)	Weight loss (%)	Group lost
[VO(tbmz)$_2$]-Y	70-150	4.5	H_2O
	150-280	5.8	nH_2O
	280-800	13.0	tbmz
[Cu(tbmz)$_2$]-Y	70-150	5.1	H_2O
	150-280	5.2	nH_2O
	280-800	13.4	tbmz

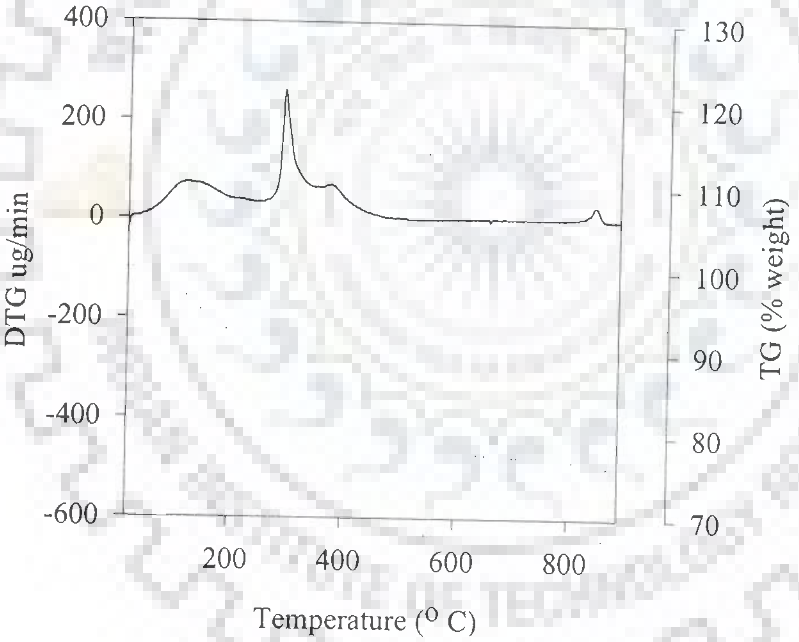


Figure 5.3. TG (dotted line) and DTG (solid line) profile of [Cu(tbmz)$_2$]-Y.

5.3.5. IR spectral studies

A partial list of IR spectral data of ligand, neat as well as encapsulated complexes are presented in Table 5.3. The intensity of the peaks in encapsulated complexes is, though, weak due to their low concentration in zeolite matrix, the spectra of encapsulated as well as neat complexes show essentially similar bands. Comparison of the spectra of these catalysts with the ligand provides evidence for the coordinating mode of ligand in catalysts. The ligand Htbmz exhibits a sharp band at 1638 cm^{-1} due to ν(C=N) (azomethine) and this band shifts to lower wave number on coordination of azomethine nitrogen to the metal ion and appears at 1626–1632 cm^{-1}. The ν(C-S) (thioalcoholic) of ligand appears at 757 cm^{-1} and this band shift towards lower wave number thereby indicating the coordination of sulfur to the vanadium[179]. Neat complex [$VO(tbmz)_2$] exhibits a sharp band at 979 cm^{-1} due to ν(V=O) stretch, while the location of such ν(V=O) band in zeolite encapsulated vanadium complex was not possible due to the appearance of a strong and broad band at ca. 1000 cm^{-1} due to zeolite frame work.

Table 5.3. IR and electronic spectral data of ligand, pure and encapsulated complexes

Compound	IR (cm^{-1})		λ_{max} (nm)
	ν(C=N)	ν(V=O)	
Htbmz	1638		205, 252, 279
[$VO(tbmz)_2$]-Y	1632	-	206, 275, 388
[$Cu(tbmz)_2$]-Y	1627		203, 312, 388
[$VO(tbmz)_2$]	1628	979	226, 246, 278, 339, 377
[$Cu(tbmz)_2$]	1626		229, 236, 274, 280, 383

5.3.6. Electronic spectral studies

Electronic spectrum of ligand Htbmz in methanol exhibits three intense bands at 205, 252 and 279 nm. The band at 279 nm is a characteristic of the presence of benzimidazole group. Usually two such bands in very close proximity due to benzimidazole group have been observed earlier [180]. Other two bands are assignable to ϕ - ϕ^* and π - π^*, respectively. In the electronic spectrum of neat complex, [$Cu(tbmz)_2$], the characteristic bands appear at 274 and 280 nm while other ligand bands appear at 229 and 236 nm. The band appearing at 300 nm is assignable to n - π* transition. In addition to this, a medium intensity band appears at 360 nm, which is assigned to ligand to metal charge transfer band. Only one characteristic band due to benzimidazole group appears at 278 nm in [VO(tbmz)$_2$] while other ligand bands appear at 226 and 246 nm. The weak shoulder band appearing at 377 nm is assignable to ligand to metal charge transfer band. Both the encapsulated complexes exhibit essentially similar spectral patterns with bands at 206, 275 and 388 nm in vanadium and 203, 312, 388 nm in copper complex. Presence of these bands confirms the existence of complexes in the cavity of zeolite-Y.

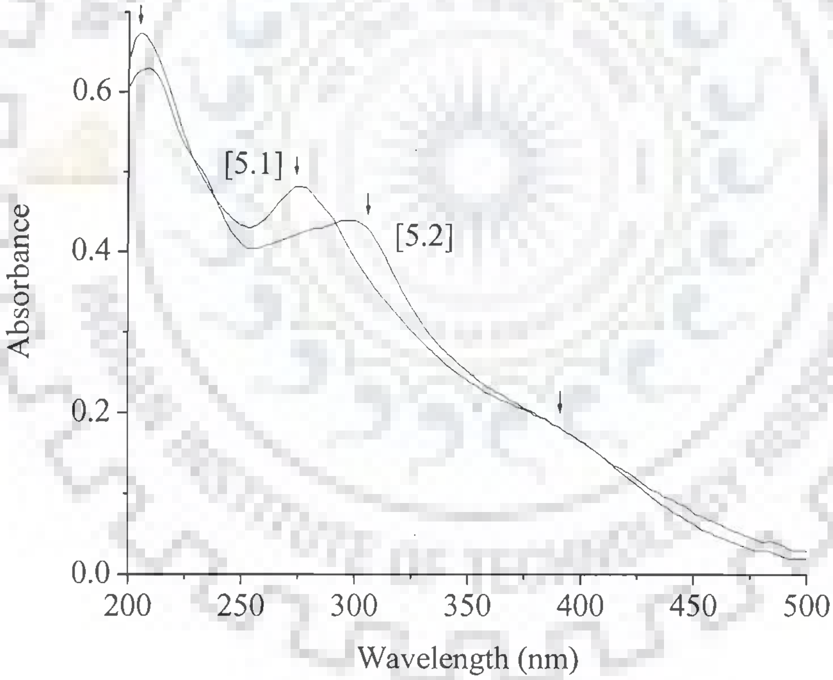
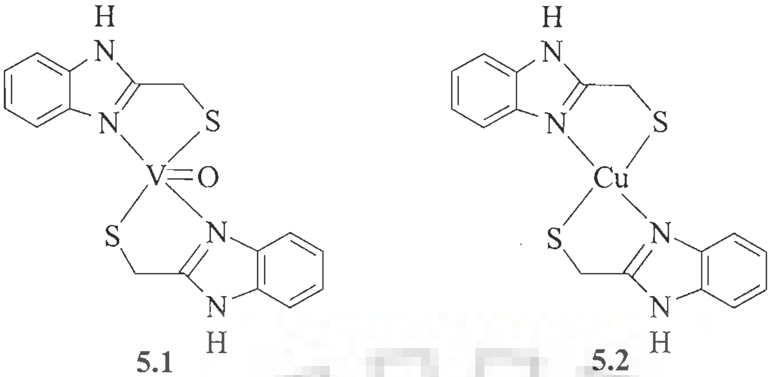


Figure 5.4. Electronic spectra of [VO(tbmz)$_2$]-Y (5.1) and [Cu(tbmz)$_2$]-Y (5.2).

On the basis of the studies presented above the following structures for the complexes encapsulated in zeolite-Y have been proposed; Scheme 5.2.



5.1 5.2

Scheme 5.2. Proposed structures for complexes

5.3.7. Catalytic activity studies

5.3.7.1. Oxidation of styrene

The oxidation of styrene was carried out by H_2O_2 using [VO(tbmz)$_2$]-Y and [Cu(tbmz)$_2$]-Y as catalysts and five oxidation products, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenyl acetaldehyde along with only minor amounts of unidentified products were obtained. These products have also been identified earlier [see previous chapters].

In search of suitable reaction conditions to achieve the maximum oxidation of styrene catalyzed by these catalysts, the effect of three different reaction parameters viz. amount of oxidant and catalyst, and temperature of the reaction mixture have been studied in details.

The effect of H_2O_2 concentration on the oxidation of styrene is illustrated in Figure 5.5. Four different H_2O_2 / styrene molar ratios of 1:1, 2:1, 3:1 and 4:1 were considered, while keeping the other parameters fixed as styrene (1.04 g, 10 mmol) and catalyst (0.035 g) in 20 ml of CH_3CN and the reaction was carried out at 80 °C. Increasing the H_2O_2 / styrene ratio increases the conversion from 39.4 % for 1:1 to 69.1 % for 2:1 and finally to 96.4 % for 3:1 molar ratio in 6 h of reaction time. No further increase in conversion was obtained beyond this molar ratio. The oxidant to substrate mole ratio of 3:1 was, therefore, considered for optimizing the other reaction conditions. For the optimization of the amount of catalyst, five different amounts of catalyst viz. 0.015, 0.025, 0.035, 0.050 and 0.075 g were considered while keeping a fixed amount of styrene (1.04 g, 10 mmol) and H_2O_2 (3.42 g, 30 mmol) in 20 ml of CH_3CN and the reaction was carried out at 80 °C. As illustrated in Figure 5.6, the conversion increases on increasing the amount of catalyst and reached to a maximum of 96.4 % with 0.035 g of catalyst while either more or less molar ratio gave lower conversions. The reason for fewer activities at higher catalyst dose may possibly be due to adsorption/chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact. Therefore, an amount of 0.035 g catalyst may be considered as appropriate to obtain the maximum conversion of styrene. Figure 5.7 illustrates the effect of oxidation of styrene at different temperatures and as observed earlier, running the reaction at 80 °C while keeping the other conditions optimized as above gave a highest conversion of 96.4 % in 6 h of reaction time. Thus, for the maximum oxidation of 10 mol of styrene other required reagents were: [VO(tbmz$_2$]-Y (0.035 g), H_2O_2 (3.42 g, 30 mmol), CH_3CN (20 ml) and temperature (80 °C).

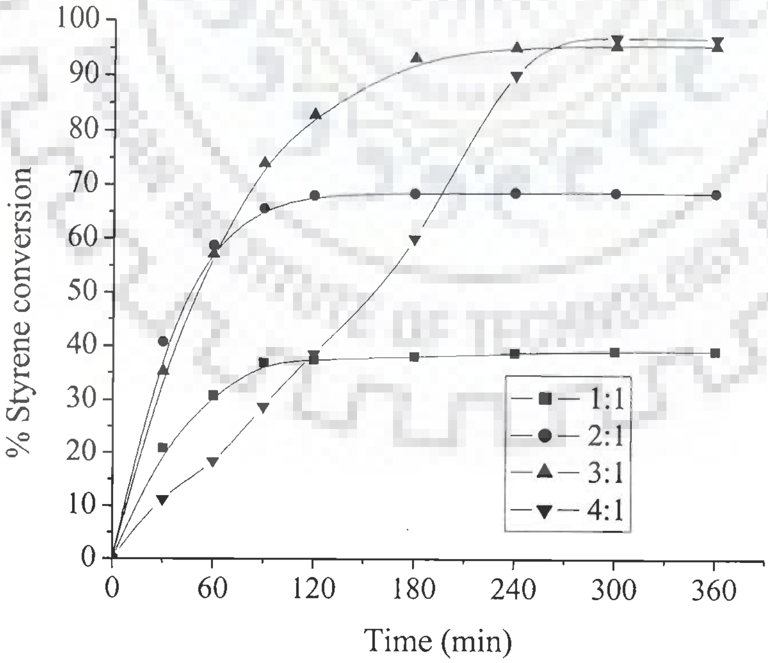


Figure 5.5. Effect of H_2O_2 concentration (H_2O_2 : styrene) on the oxidation of styrene.

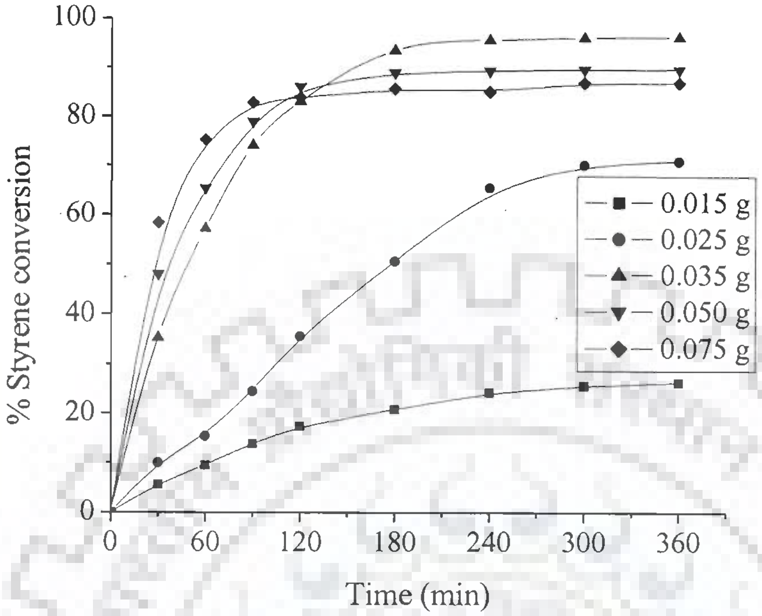


Figure 5.6. Effect of amount of catalyst on the oxidation of styrene.

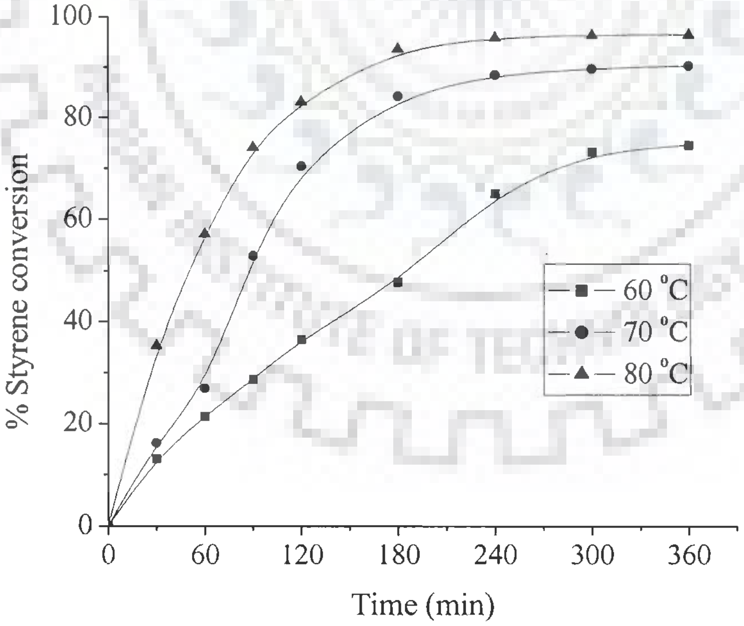


Figure 5.7. Effect of temperature on the oxidation of styrene.

After acquiring the optimized reaction conditions for [VO(tbmz)$_2$]-Y, catalyst [Cu(tbmz)$_2$]-Y was also tested using same reaction conditions. Figure 5.8 compares the efficiency of both catalysts as a function of time while Table 5.4 provides conversion percentage of styrene and selectivity details of various products. It is clear from the table that the performance of [Cu(tbmz)$_2$]-Y is much poorer in comparison to that of [VO(tbmz)$_2$]-Y and only four products namely, styrene oxide, benzaldehyde, benzoic acid and phenylacetaldehyde are identified as a result of oxidation. Amongst the different products formed by the two catalysts, the selectivity of styrene oxide is better for [Cu(tbmz)$_2$]-Y (12.9 %) than [VO(tbmz)$_2$]-Y (6.1 %), while both catalysts gave benzaldehyde in highest yield. The yields of other products are much smaller and are comparable. The mechanism for the oxidation of styrene and the formation of oxidation products have been discussed earlier in details [see chapter 2].

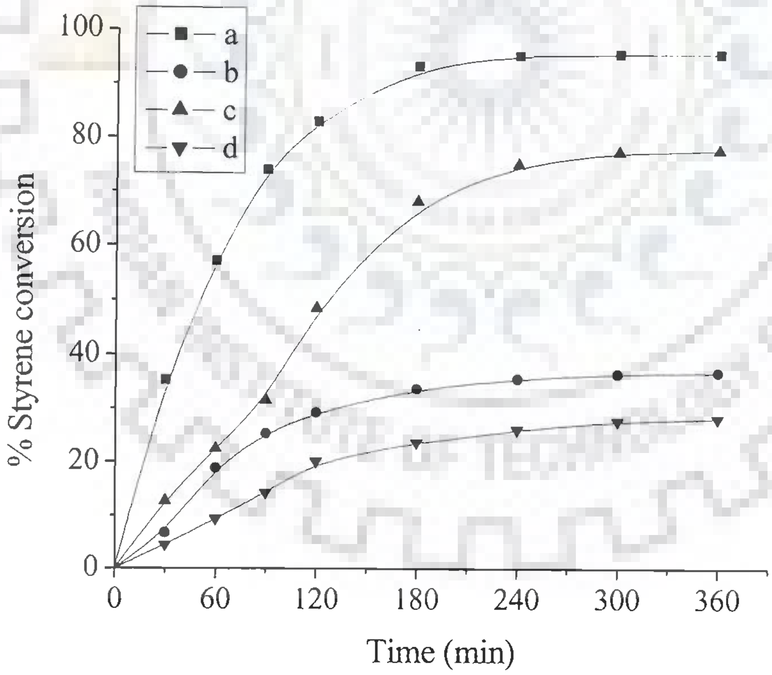


Figure 5.8. Catalytic comparison of catalysts for the oxidation of styrene with H_2O_2 as oxidant: [VO(tbmz)$_2$]-Y (a), [Cu(tbmz)$_2$]-Y (b), [VO(tbmz)$_2$] (c) and [Cu(tbmz)$_2$] (d).

Table 5.4. Products selectivity and percent conversion of styrene with H_2O_2 as oxidant after 6 h of reaction time

Catalyst	% Conv.	TOF (h^{-1})[a]	% Product selectivity					
			so	bza	phed	bzac	phaa	Other
[VO(tbmz)$_2$]-Y	96.4	205.4	6.1	68.1	12.4	9.6	2.3	1.5
[Cu(tbmz)$_2$]-Y	36.9	43.3	12.9	74.8	-	8.2	2.9	1.2
[VO(tbmz)$_2$]	78.3	166.8	5.4	70.6	11.5	8.3	2.6	1.6
[Cu(tbmz)$_2$]	28.3	33.2	10.7	73.2	-	10.6	3.4	2.1

[a]TOF h^{-1} (Turn over frequency): moles of substrate converted per mole of metal ion (in the solid state catalyst) per hour

Neat complexes, [VO(tbmz)$_2$] and [Cu(tbmz)$_2$] were also tested for the oxidation of styrene using same mole concentration of complex as in their respective zeolite encapsulated ones under above reaction conditions. The conversion details are also presented in Figure 5.8 and Table 5.4. Neat complexes exhibited lower conversions than their encapsulated analogues. However, the formation of the products and their activity order are same as obtained by respective encapsulated complexes.

Under the above optimized reaction conditions, catalytic action of [VO(tbmz)$_2$]-Y and [Cu(tbmz)$_2$]-Y along with their neat analogues have also been tested using TBHP as an oxidant i.e. 30 mmol 70 % TBHP and 0.035 g catalyst for 10 mmol styrene were taken in 20 ml of CH_3CN and reaction was carried out at 80 °C. Neat complexes have also been tested using same mole concentrations as taken for respective encapsulated complexes. Figure 5.9 provides the percentage conversion as a function of time and Table 5.5 compares the selectivity data along with the conversion percentage and turn over frequency (TOF) after 6 h of reaction time. It is clear that under the optimized conditions, the obtained percentage conversion varied in the order: [Cu(tbmz)$_2$]-Y (48.2%) > [Cu(tbmz)$_2$] (34.7%) > [VO(tbmz)$_2$]-Y (22.4%) > [VO(tbmz)$_2$] (13.6%). Thus, the conversion of styrene with all these catalysts are relatively low but the selectivity of the formation of styrene oxide is considerably high (52.6 to 57.7 %) whereas, the selectivity of benzaldehyde is low (38.2 to 42.7 %). Only small amount of the formation of other products is possibly due to no further oxidation of styrene oxide to other oxidized products as observed above due to the mild oxidizing nature of TBHP.

Table 5.5. Products selectivity and percent conversion of styrene with TBHP as oxidant after 6 h of reaction time

Catalyst	% Conversion	TOF (h^{-1})	% Product selectivity		
			so	bza	Other
$[VO(tbmz)_2]$-Y	22.4	47.7	55.5	38.6	5.9
$[Cu(tbmz)_2]$-Y	48.2	56.6	57.7	38.2	4.1
$[VO(tbmz)_2]$	13.6	28.9	52.6	42.7	4.7
$[Cu(tbmz)_2]$	34.7	40.7	53.3	41.1	5.6

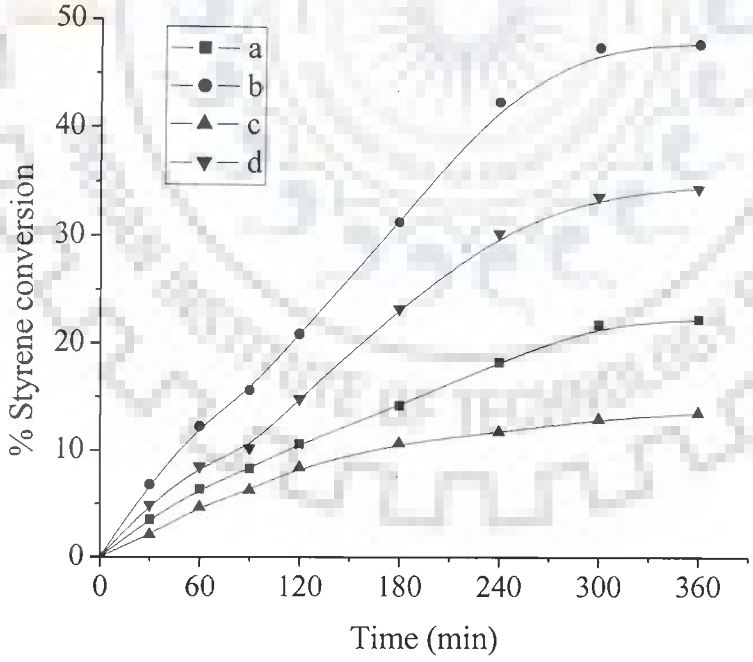
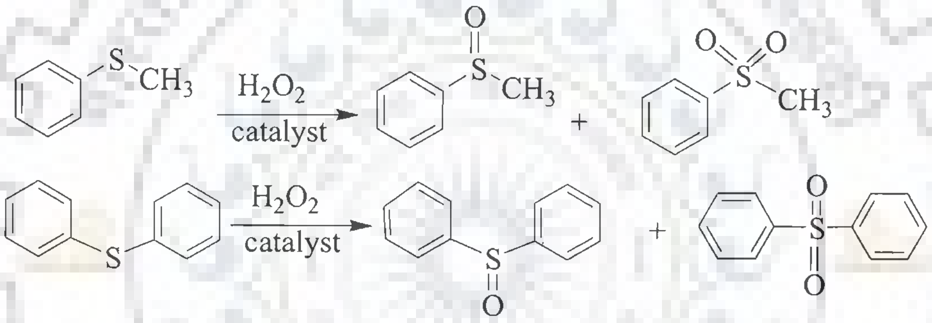


Figure 5.9. Catalytic comparison of catalysts for the oxidation of styrene with TBHP as oxidant : $[VO(tbmz)_2]$-Y(a), $[Cu(tbmz)_2]$-Y(b), $[VO(tbmz)_2]$ (c) and $[Cu(tbmz)_2]$ (d).

Comparison of the catalytic potential of these catalysts with the catalysts reported in Chapter 4 reveal that vanadium complexes have very good catalytic activity, whereas, the selectivity of the styrene oxide is much better with TBHP.

5.3.7.2. Oxidation of methyl phenyl sulfide and diphenyl sulfide

The sulfur atom of the diphenyl sulfide and methyl phenyl sulfide is electron rich and has been shown to undergo electrophilic oxidation to give sulfoxide. Such oxidation of methyl phenyl sulfide and diphenyl sulfide by aqueous 30 % H_2O_2 has been carried out using $[VO_2(tbmz)_2]$-Y and $[Cu(tbmz)_2]$-Y as catalyst. Scheme 5.3 presents the oxidation products of both sulfides.



Scheme 5.3

Again, reaction conditions have been optimized for the maximum oxidation of diphenyl sulfide considering $[VO(tbmz)_2]$-Y as a representative catalyst and two different parameters, viz. amounts of oxidant and catalyst were varied.

The effect of H_2O_2 concentration on the oxidation of diphenyl sulfide is illustrated in Figure 5.10. Using three different concentrations of aqueous 30 % H_2O_2 viz. 5 mmol (0.057 g), 10 mmol (1.14 g) and 15 mmol (1.7 g) for the fixed amount of diphenyl sulfide (0.93 g, 5 mmol) and $[VO(tbmz)_2]$-Y (0.025 g) in CH_3CN (10 ml), the obtained percent conversion of diphenyl sulfide were 24.6, 70.6 and 91.7 %, respectively, in 7 h of reaction time at ambient temperature. No further improvement in the conversion was noted above this molar ratio. Similarly for four different amounts (viz. 0.005, 0.015, 0.025 and 0.035 g) of catalyst and at H_2O_2 to diphenyl sulfide molar ratio of 3:1 under above reaction conditions, 0.025 g of catalyst gave a good conversion of 91.7 % while 0.035 g catalyst has shown only slight improvement in the conversion; Figure 5.11. Thus, 0.025 g catalyst may be considered sufficient enough to run the reaction under above conditions.

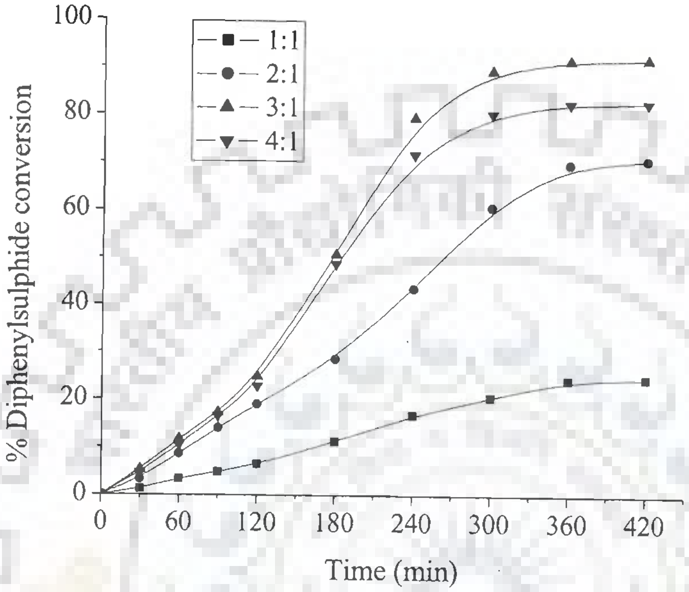


Figure 5.10. Effect of H_2O_2 concentration (H_2O_2 : diphenyl sulfide) on oxidation of diphenyl sulfide.

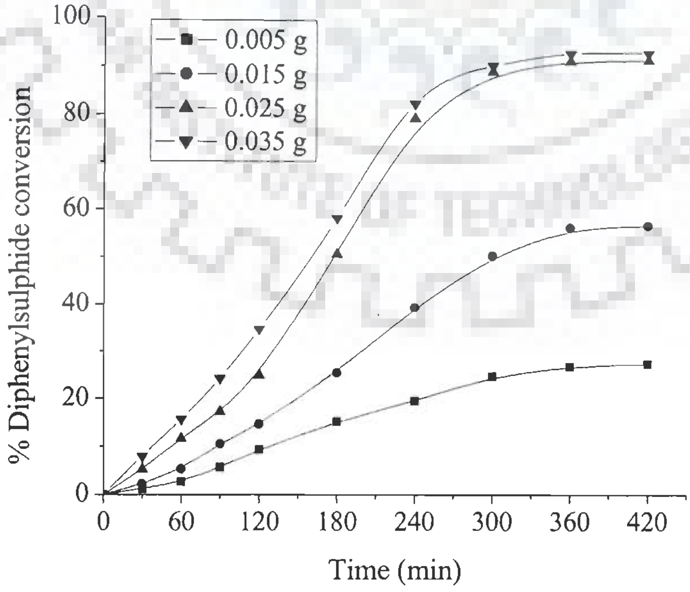


Figure 5.11. Effect of catalyst amount on oxidation of diphenyl sulphides.

While carrying out the oxidation of methyl phenyl sulfide under above optimized conditions, it was observed that the substrate to H_2O_2 molar ratio of 1:1, was sufficient enough to give 94.3 % conversion within 3 h of contact time. Increasing the amount of oxidant to 2:1 (oxidant : substrate) molar ratio caused only marginal increment in the conversion. Thus, the substitution of benzene in place of methyl group slows down the conversion. Selectivity details for the obtained products are presented in Table 5.6. It is clear from the table that catalyst [VO(tbmz)$_2$]-Y has good catalytic potential for both substrates with high turn over frequency. But the selectivity for the formation of methyl phenyl sulfoxide is better (88.9 %) than for diphenyl sulfoxide (72.9 %).

The catalytic activity of neat complexes using same mole concentration as used for encapsulated complexes under above reaction conditions have also been tested for comparison. Figure 5.12 compares the conversion of diphenyl sulfide with neat as well as encapsulated complexes while Figure 5.13 compares the conversion of methyl phenyl sulfide. As presented in Table 5.6, neat complex exhibited only comparable conversion to that of encapsulated one. The uniform dispersal of active metal centers in the zeolite matrix prevents the loss of catalytic activity thus showing better catalytic results.

Table 5.6. Percent conversion of sulfides along with TOF and products selectivity data

Catalyst	Substrate	% Conv. / time	TOF (h^{-1})	% Selectivity	
				sulfoxide	sulfone
[VO(tbmz)$_2$]-Y	Diphenyl sulfide	91.7/7h	117.2	72.9	27.1
[VO(tbmz)$_2$]-Y	Methyl phenyl sulfide	94.3/3h	281.2	88.9	11.1
[VO(tbmz)$_2$]	Diphenyl sulfide	73.6/7h	94.1	77.8	22.2
[VO(tbmz)$_2$]	Methyl phenyl sulfide	82.4/3h	245.7	90.3	9.7

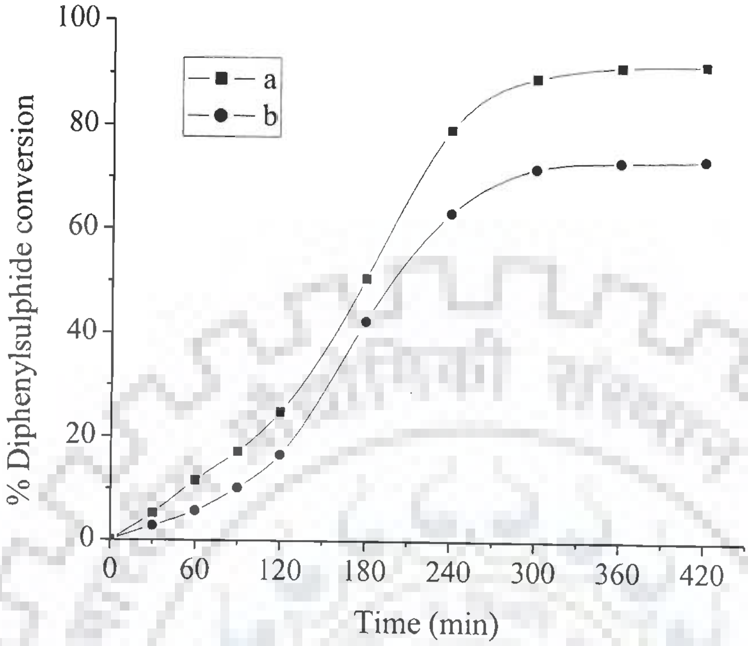


Figure 5.12. Catalytic comparison of catalysts for the oxidation of diphenylsulphide: [VO(tbmz)$_2$]-Y(a), [VO(tbmz)$_2$] (b).

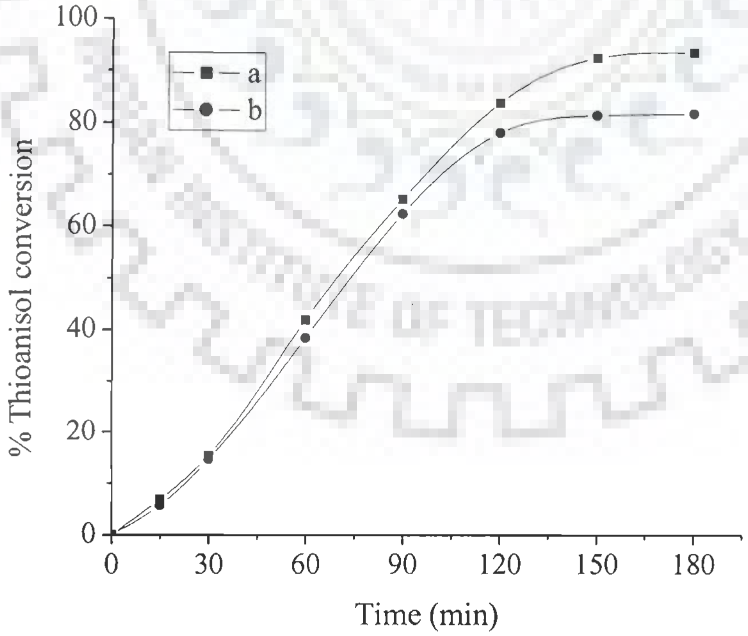


Figure 5.13. Catalytic comparison of catalysts for the oxidation of thioanisol: [VO(tbmz)$_2$]-Y(a), [VO(tbmz)$_2$] (b).

5.3.8. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the neat complexes dissolved in methanol were treated with H_2O_2 dissolved in methanol and the progress of the reaction was monitored by electronic absorption spectroscopy. Thus, the titration of [VO(tbmz)$_2$] dissolved in methanol (ca. 10^{-4} M solution) with one-drop portions of 30 % H_2O_2 resulted in the quick disappearance of 246 nm band while a slow increase in the intensity of 223 nm band was observed. The band appearing at 278 nm gradually shifts to 276 nm with increase in band maximum and the band at 377 nm splits into two bands which appear at 339 and 384 nm with slight increase in intensity (see inset of Figure 5.14). These spectral changes and the presence of isosbestic at 325 nm suggest the interaction of oxovanadium(IV) complex with H_2O_2 possibly to give oxoperoxovanadium(V) species. The spectral changes are presented in Figure 5.14.

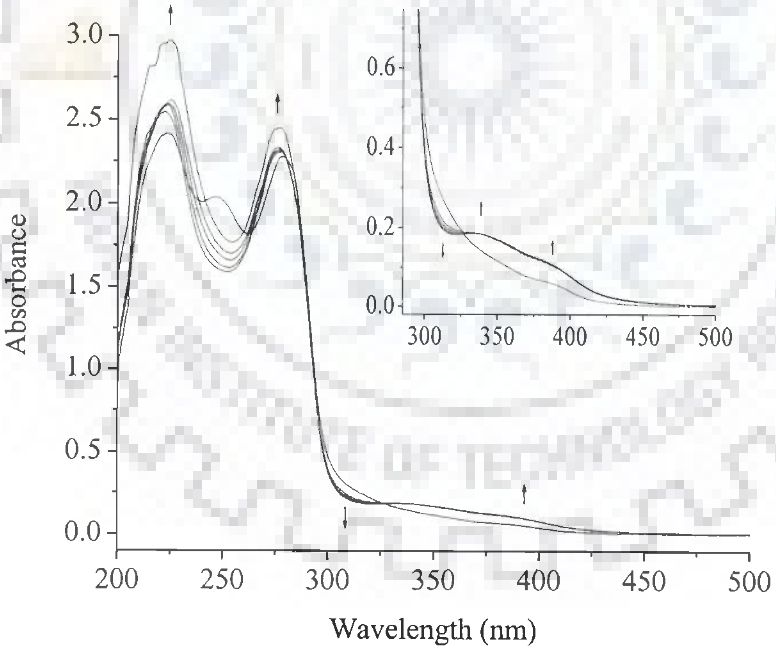


Figure 5.14. Titration of [VO(tbmz)$_2$] with H_2O_2. The spectra were recorded after successive addition of one drop portions of H_2O_2 in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of [VO(tbmz)$_2$] in methanol.

As shown in Figure 5.15, the addition of one-drop portions of 30 % H_2O_2 dissolved in methanol to a methanolic solution of [Cu(tbmz)$_2$] (ca. 10^{-4} M solution) resulted in the gradual increment of the intensity of bands appearing at 274 and 280 nm. Other band appearing at 229 nm shifts slowly to 236 nm with increase in band maximum while the band at 300 nm slowly broadens with slight increase in intensity. A very week shoulder band appearing at 382 nm slowly disappears (see inset of Figure 5.15). No other bands could be located in the visible region beyond this point. It was, therefore, not possible to have idea about the change in the d – d transition band(s) due to H_2O_2 titration. However, the spectral changes in the UV region on treatment with H_2O_2 suggests the formation of intermediate peroxo species which finally transfers oxygen to the organic substrates.

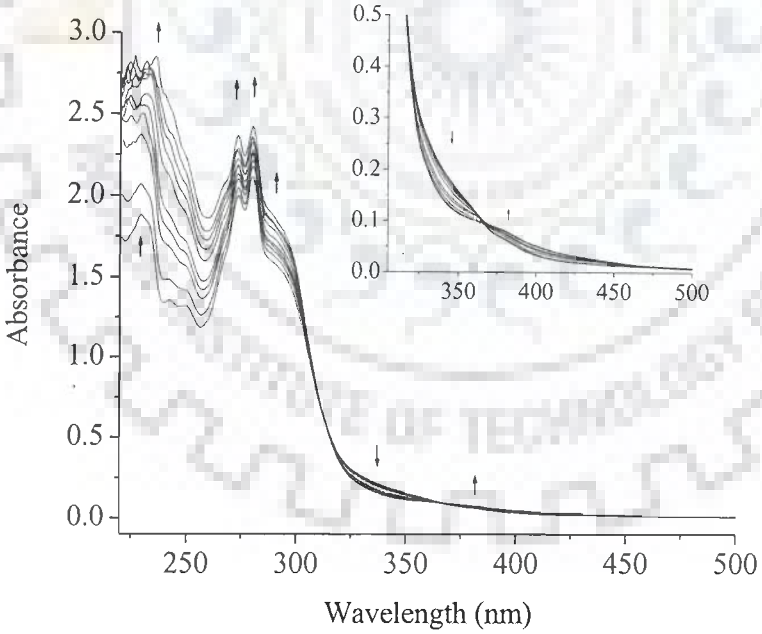


Figure 5.15. Titration of [Cu(tbmz)$_2$] with H_2O_2. The spectra were recorded after successive addition of one drop portions of H_2O_2 in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of [Cu(tbmz)$_2$] in methanol.

5.3.9. Test for recycle ability and heterogeneity of the reactions

The recycle ability of both the encapsulated complexes has been tested. For styrene, the reaction mixture after a contact time of 6 h was filtered and after activating the catalysts by washing with acetonitrile and drying at ca. 120 °C, they were subjected to further catalytic reaction under similar conditions. No appreciable loss in catalytic activity suggests that complexes are still present in the cavity of the zeolite-Y. The filtrate collected after separating the used catalysts was placed into the reaction flask and the reaction was continued after adding fresh oxidant for another 4 h. The gas chromatographic analysis showed no improvement in conversion. Similar results were also obtained with other substrates. All these confirm that the reactions did not proceed upon removal of the solid catalysts. The reactions were, therefore, heterogeneous in nature.

5.4. CONCLUSIONS

Encapsulation of oxovanadium(IV) and copper(II) complexes of monobasic bidentate NS donor ligand, 2-mercaptomethylbenzimidazole (Htbmz) in the cavity of zeolite-Y by flexible ligand method have been described. These complexes have been characterized by various physico-chemical methods. The encapsulated complexes, [VO(tbmz)$_2$]-Y and [Cu(tbmz)$_2$]-Y have been used as catalysts for the oxidation of styrene, methyl phenyl sulfide and diphenyl sulfide. Under the optimized reaction conditions, [VO(tbmz)$_2$]-Y gave 96.4 % conversion of styrene with five oxidation products, styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde. Conversion with [Cu(tbmz)$_2$]-Y is considerably low (36.9 %) and gave only four products, styrene oxide, benzaldehyde, benzoic acid and phenylacetaldehyde. In both cases formation of benzaldehyde is relatively high. These catalysts are very active for the oxidation of methyl phenyl sulfide and diphenyl sulfide. The oxidation of diphenyl sulfide required at least H_2O_2 to diphenyl sulfide ratio of 3:1 to give 91.7 % conversion in 7 h of reaction time. However, 94.3 % conversion of methyl phenyl sulfide has been achieved within 3 h of contact time at a substrate to H_2O_2 ratio of 1:1. The catalytic activity of neat complexes using similar molar concentration as that used for encapsulated complexes under above reaction conditions have also been tested for comparison. It has been observed that the corresponding neat complexes have shown equally good catalytic activities. However higher turn over frequencies and recyclability make the zeolite-encapsulated complexes better than their neat analogues.

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SUMMARY & CONCLUSIONS

Summary and conclusions

Present thesis highlighted the importance of zeolite encapsulated metal complexes and their catalytic potentials for various organic transformations. The applications of zeolite encapsulated metal complexes have further been extended in this thesis. The main objective of the thesis set out was to synthesize new zeolite encapsulated metal complexes and study their catalytic utility for various oxidation reactions. This goal has been achieved by synthesizing zeolite-Y encapsulated metal complexes, [VO_2(sal-ambmz)]-Y, [Cu(sal-ambmz)Cl]-Y (Hsal-ambmz = Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole), [VO(sal-dach)]-Y, [Cu(sal-dach)]-Y (H_2sal-dach = Schiff base derived from salicylaldehyde and 1,2-diaminocyclohexane), [VO(sal-oaba)(H_2O)]-Y, [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)(H_2O)$_3$]-Y (H_2sal-oaba = Schiff base derived from salicylaldehyde and *o*-aminobenzyl alcohol), [VO(tbmz)$_2$]-Y and [Cu(tbmz)$_2$]-Y (Htbmz = 2-mercaptomethylbenzimidazole). These complexes have been characterized by metal analyses, spectral (FT-IR and electronic) studies, scanning electron micrographs and powder X-ray diffraction as well as thermal analysis patterns. The respective neat complexes have also been prepared and characterized by various physico-chemical studies. The formulations of the encapsulated-complexes have been inferred on the basis of respective neat complexes and conclusions drawn from the various characterization studies.

Catalytic activities of all these encapsulated complexes have been studied for the oxidation of styrene using H_2O_2 and *tert*-butyl hydroperoxide. The oxidation of styrene gave five reaction products namely, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde. Benzaldehyde has been obtained in major and styrene oxide in minor yield using H_2O_2 as oxidant while the yield of styrene oxide was improved significantly with *tert*-butylhydroperoxide. The oxidation of phenol yielded catechol and *p*-hydroquinone with good selectivity towards catechol. The oxidation of cyclohexene catalyzed by [VO(sal-dach)]-Y, [Cu(sal-dach)]-Y gave cyclohexeneoxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one and cyclohexane-1,2-diol as major products. A maximum of 96.1 % conversion of methyl phenyl sulfide with [VO_2(sal-ambmz)]-Y) and 91.0 % with [Cu(sal-ambmz)Cl]-Y has been observed in which the selectivity of major product methyl phenyl sulfoxide has been found to be ca. 98 %. The oxidation of diphenyl sulfide required at least H_2O_2 to diphenyl sulfide ratio of 3:1 to give 91.7 % conversion in 7 h of reaction time. A maximum of 78.1 % conversion of cyclohexane catalysed by [Cu(sal-dach)]-Y while only 21.0 % conversion by [VO(sal-dach)]-Y with major reaction products of cyclohexanone, cyclohexanol and cyclohexane-1,2-diol have been obtained. All these reactions were carried out under optimized reaction conditions and reaction products were identified by GC and their identities were confirmed by GC-MS. Possible reaction pathways for all these catalytic reactions have been concluded by reacting neat complexes with H_2O_2 in suitable solvent and monitoring the spectral changes by electronic spectrometer.

The catalytic activities of these complexes have also been compared with the corresponding free complexes and it has been observed that some of the free complexes have comparable catalytic activities. However, the recycle ability and easy separation of the encapsulated-catalysts from the reaction mixture make zeolite-encapsulated metal complexes better catalysts over neat ones. Besides, these complexes are stable and do not leach during catalytic actions in solution.

Thus, synthesis and characterization of zeolite-encapsulated metal complexes and their catalytic potentials presented in the thesis contribute considerably to the existing knowledge. It is hoped that these catalysts may find industrial applications in near future.

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