REPORT OF THE PROJECT

ENTITLED

Catalysis by Neat& Supported Complexes in Industrial Oxidation Reactions : - A Comparative Study

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Dr. Pearly Sebastian Chittilappilly
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Chapter 1

Introduction

Coordination chemistry comprises a large body of inorganic chemistry research. It is the chemistry of metal complexes and has fascinated and inspired the chemists all over the world. There is an ever increasing academic, biochemical and commercial interest on the metal complexes of organic chelating agents. This has resulted in the emergence of allied fields like organometallic chemistry, homogeneous catalysis and bioinorganic chemistry.

1.1 Schiff Base Complexes

Metal complexes of Schiff bases have occupied a central place of importance in the development of coordination chemistry. Recent years have witnessed a great deal of interest in the research of different types of Schiff base complexes of transition elements[1-4]. The interest in the design and synthesis of novel transition metal complexes containing Schiff bases lies in their biological and catalytic activity in many reactions [5,6]. Depending on the nature of the Schiff base ligands, there are immense applications of their complexes in the chemical field. Synthesis and design of the metal complexes with desired properties is still a developing field. Transition metal complexes of many Schiff bases are found to satisfy the requirements for acting as catalysts for the oxidation of organic substrates[7,8]. Transition metal complexes have wide applications in food industry, dye industry, analytical chemistry, catalysis, agrochemical and biological activities [9]. Many Schiff base metal chelates catalyse reactions like hydrolysis, carboxylation, decarboxylation, elimination, aldol condensation, redox reactions [10,11].
In the development of coordination chemistry metal complexes of Schiff bases have occupied a central place of importance. Schiff bases are very diverse and when a complexation reaction with a metal ion occurs, they form a five or six membered chelate ring.

The Schiff base ligands exert profound influence on the activity of the metal centre. Schiff base containing poly functional groups have produced stable metal complexes of transition and inner transition metal ions. These ligands and their metal complexes have also played a significant role in the domains of stereo chemistry, structure, isomerism, magnetism, spectroscopy, kinetics and mechanism of reaction, reaction of coordinated ligands, catalysis, pigments and dyes, model systems of biochemical interest, stabilizers, electro optical devices, agriculture and polymers. Many Schiff base complexes are found to have anti-inflammatory[12] antibiotic[13], antimicrobial [14], anti-tumor activity [15].

Schiff bases with variable donation sites could be monodentate, bidentate, tridentate or tetradeutate forming mono or polynuclear complexes. The tetradeutate Schiff base complexes are employed to design metal complexes related to synthetic and natural oxygen carriers. Complexes of Schiff bases with oxygen and nitrogen as donor atoms were found to be very effective reagents aiding the oxidation of alcohols and alkenes [16]. The coordination chemistry of Schiff base complexes are widely investigated since they provide ample opportunities for inducing substrate chirality, tuning metal centered electronic factor and enhancing solubility and stability of both homogeneous and heterogeneous catalysts [17-22]. The complexing ability of Schiff base is due to the presence of azomethine linkage. The azomethine group has a tendency to donate the lone pair of electrons present on the nitrogen atom of the azomethine moiety(C = N-). Presence of another donor group close to azomethine group increases the coordinating effect of the lone pair of electrons, thereby increasing the stability of the metal complexes. The stability of Schiff
base complexes depends upon the strength of C=N bond, basicity of amino group and steric factors. The presence of electron withdrawing ring system in the ligand decreases the availability of the lone pair of electrons.

The field of medicine has witnessed an increase in the number of complexes with therapeutic value. Cobalt(III) Schiff base complexes are potential antiviral agents, cis-dichloro diamine platinum(II) is an anti-cancer agent and copper(II) Schiff base complex is anti tubercular agent. The use of atom transfer radical cyclization is mediated by copper(II) Schiff base complexes to furnish nitrogen hetero cycles most of which are biologically active molecules. The use of copper Schiff base catalyst in carbon based cyclization reaction were recently discovered.

Schiff base complexes having oxygen coordination is important both structurally and biologically. These type of compound include Schiff base complexes derived from semi carbazide, amino phenols etc.

The factors that influence the stability of complexes are
i) the presence of chelate  ii) the size of chelate ring iii) steric factors iv) resonance effects.

The scope of this field is increasing because of the use of these compounds as catalysts in industrial processes like oxo process, Monsanto process etc. The present investigation is based on the synthesis and characterization of neat and encapsulated complexes of transition metals with Schiff bases. Some of the Schiff base complexes with heterocyclic ring was selected.

Copper(II) Schiff base complexes are found to act as catalysts for the oxidative coupling of phenols [23]. They also act as catalysts for the oxidation of phenols to quinones. These complexes usually form adducts with oxygen molecules. Information about many such complexes which can be bound reversibly with dioxygen are available in the review by Basolo etal [24]. Cobalt(II) complexes of aromatic Schiff bases form oxygenated complexes at
lower temperatures (-OOC) possibly because these Schiff bases can readily donate electron density to the metal ion. Cobalt(II) complexes with the Schiff base ligand such as Co(Salen) [where Salen = N,N’-bis(salicylaldehyde) ethylenediimine dianion] and its analogues have been the first and most extensively investigated as reversible oxygen carriers [25-27]. The reversible binding of molecular oxygen to transition metal complexes can modify their properties to a great extent [28]. The mixed ligand complexes of transition metals containing ligands with N, S and N, S, O donors show interesting stereochemical, electrochemical and electronic [29] properties. The one reaction that requires special mention is the enantioselective electrocatalytic epoxidation of olefins in the presence of chiral Schiff base complexes of manganese [30].

1.1 Catalysis

Catalysis is an area of prime importance in the frontier area of chemistry. A thermodynamically favorable reaction may be slow at modest temperature and so not at all valuable for synthesis. The rate can be accelerated by increasing the temperature. But providing energy to do so may be expensive and induce side reactions that will affect the product yield. A more attractive approach to increase the rate of a reaction is the use of catalysts. A catalyst can accelerate a thermodynamically allowed reaction by lowering the energy barrier. The basic characteristics essential for a catalyst are high activity, good selectivity and regenerability. Nowadays all the products manufactured utilize the rate enhancement and energy saving property of catalysts in the various steps of their industrial production. The industrial reactions accelerated by the presence of a catalyst are associated with the production of a large quantity of inorganic effluents, which are difficult to dispose off. One of the major concerns in the field of catalysis is the minimization of waste production in various chemical processes.
The growing demands for the design of environment friendly products and processes have led to the development of green chemistry. In view of the growing concern over environmental pollution and with further advance of catalytic sciences, chemical industries are forced to adopt new safe and eco-friendly technologies with less consumption of energy and raw materials. Chemical reactions involving catalysis are more preferred as they are highly effective under milder conditions and generate minimum wastes. Thus there is a constant urge for the need to develop regenerable and effective solid catalysts.

Molecular design techniques, in which organic and inorganic surfaces are chemically modified, revolutionized scientific world increasing their usefulness in catalytic field. The modified materials have considerable potential as alternatives to conventional homogeneous and heterogeneous catalysts. Scientists are in a way to explore new techniques and compounds which could give promising results in various biological and industrial field. Properties of the compounds are tuned by altering the positions and nature of atoms or radicals to satisfy our needs. This outlook has resulted in the production of several compounds with wide range of applications in various fields. Literature survey supports this fact.

Basically there are three different fields of catalysis: homogeneous, heterogeneous and biological (enzymatic) catalysis. Homogeneous catalysts include transition metal complexes existing in a series of oxidation states and acting as good catalysts for many chemical reactions. The disadvantages associated with them have put greater emphasis on the development of new and improved heterogeneous catalytic systems. Actually, studies in area of supported transition metal complexes are taking wide attention due to their various advantages. Heterogenization of metal complexes known to be active in homogenous catalysis can be achieved by (i) immobilization of the metal complex on insoluble support e.g., polymers, (ii) encapsulating it in the nanocavity of zeolites and (iii) polymerization of metal complexes.
Interest in inorganic supports has arisen because of their unique characteristics of flexibility and stability. Inorganic supported catalysts by means of their rigid structure can act as bio-functional catalysts [31]. Of all the supports used, the use of zeolite molecular sieves has gained considerable importance due to their ability to tailor the structure of the catalyst to maximize their activity [32,33]. The process of encapsulation provides a simple way of coupling the reactivity of transition metal complexes with the robustness and stereochemistry of zeolite.

Nowadays researchers are actively engaged in encapsulating the metal complexes in the cavities of zeolites and other suitable molecular sieves which may be used as industrial and biomimetic catalysts [34,35]. The most widely used technique to heterogenize complexes is to encapsulate them in zeolite pores. The supported complexes possess several advantages when compared to their homogeneous counterparts. Since the catalyst trapped in zeolite cavity, products can be easily separated. Keeping in mind the different commercial benefits associated with the heterogenization of complexes, efforts are being made to develop relatively new zeolite catalysts for providing a break through in the industrial field of active and selective organic transformations [36-38]. With this view, a large number of Schiff base complexes have been synthesized inside zeolite cages and studied.

1.2 Zeolite encapsulated complexes

Zeolites are crystalline aluminosilicates with an open lattice framework and contain silica and alumina tetrahedra joined through oxygen bridges to form a three dimensional structure. They belong to the tetrasilicate family of minerals [39-41]. The interconnection of Si and Al tetrahedra through oxygen bridges play a major role in enhancing the thermal stability of the molecule. The zeolite structure is found to be stable even at higher temperatures of about 700°C [42].
The primary building units of tetrahedra can arrange themselves in different ways to form different rings of various dimensions. These rings are joined together to form complex secondary building units. The general formula of the zeolite structure is \( \text{M}^{n+} \times n(\text{Al}, \text{Si}, \text{O}_{2x+2y})^{x-} \). The charge carried by the tetrahedral Al framework is found to be neutralized by the \( \text{M}^{n+} \) cation\[43\]. The open structure helps them to take up water and other small molecules in their interstices reversibly but not the complex or bigger molecules such as methane and ethane. Thus they act as molecular sieves. The potential for coupling the shape selectivity associated with the well defined channels and cages of zeolites with the reactivity of metal complexes makes these molecular sieves particularly attractive as solid supports. In zeolite, cations move freely through the open structure and can be exchanged reversibly with other cations.

Barrer and Daney reported the synthesis of zeolites by adding a tetra alkyl ammonium salt to the reaction mixture and allowing it to crystallize slowly at a temperature above 100ºC. This reaction yield zeolites with controllable pore size. The pore structure is determined by the selection of the organic base which remains trapped inside and can be removed by heating the zeolite to 400 - 500ºC. The \( \text{Na}^+ \) ions present in the solution was retained by the zeolite as the counter ions that may be converted to the proton form by ion-exchange with strong mineral acids.

The channel or pore size of the zeolite is controlled by the number of oxygen atoms that form a ring like entry to the channels. These rings may consist of 8, 10 or 12 oxygen atoms as reaction centers for binding and catalysis of molecules. The ligand molecules coordinated to the metal tunes the selectivity of the catalyzed reactions. Schiff base complexes are of particular importance in this area. Several zeolite encapsulated salen complexes of transition metal were known to be catalytically active in oxidation reaction [44-47].
Zeolites have a distinct advantage over conventional support materials in that a metal complex can be physically trapped in the pores and not necessarily bound to the oxide surface. A metal complex of the appropriate dimensions might be encapsulated in a zeolite yet be free to move within the confines of a cage or channel. This could be viewed as a bridge between a homogeneous and heterogeneous system. The porous inorganic mantle zeolite provide the right steric requirement for the metal complexes and impose certain restrictions based on size and shape to the access of the active site by the substrate molecules.

The synthesis of the transition metal complexes inside the zeolite super cage has an added advantage that they create a favorable condition for reversible addition of molecular oxygen and decreases considerably the oxidation of the central metal ion. Zeolite encapsulated complexes are receiving wider attention in the field of catalysis. The zeolite pores act as reaction centers for binding and catalysis of molecules [48,49]. With this view zeolite encapsulated cobalt tetramethylporphyrin complex was prepared and studied its dioxygen binding property [50]. Some copper(II) and manganese(II) Salen complexes confined to X and Y zeolites showed good performance as catalysts in the decomposition of H₂O₂ and tert-butylhydroperoxide [51]. So these encapsulated catalysts were used in the oxidation of phenol and styrene. They are found to be well catalyzing in the oxidation reaction of p-xylene and are found to be thermally stable.

The cis-manganese(II) bis-2,2'-bipyridyl complex encapsulated in zeolite X or Y are reported to be very good catalysts for the selective alkene oxidation [52]. They showed moderate to high conversion and selectivity towards the oxidation of a variety of olefinic substrates even at room temperature. The above-mentioned catalysts were active in the oxidation of cyclohexene for up to 1000 cycles with H₂O₂. Repeated catalyst regeneration is possible in these cases. Zeolite Y Mn(III) Salen complexes catalyze oxidation reactions using
iodosylbenzene as the oxidant [53]. An increase of turnover numbers by 200 fold on using a zeolite encapsulated iron phthalocyanine complex has been observed for the oxidation of n-octane [54]. Tatsumi and et al. used H₂O₂ as an efficient oxidant for alkenes in the presence of the zeolite Y encapsulated manganese tetramethylporphyrin [55]. Bein and et al. have reported the encapsulation of methyltriiodorhenium in zeolite Y host and the activity of the resulting hybrid catalysts for olefin metathesis [56]. Intrazeolite complex of manganese trimethyltriazacyc1ononane is found to be a highly selective epoxidation catalyst for a number of olefins with H₂O₂ [57].

Zeolite encapsulated Schiff base complexes can also act as catalysts for hydrogenation reactions [58-61]. Although Pd(II) salen complex catalyzes the hydrogenation of alkene, substrate selectivity is less [62]. But encapsulated Pd(II) salen complex show selectivity towards linear alkene. Zeolite Y encapsulated Ni (salen) complex were reported to have similar selectivity for the hydrogenation of hexane -1 in the presence of cyclohexene.

1.3 SCOPE OF THE PRESENT INVESTIGATION

Study of the catalytic activity of the neat and encapsulated complexes may reveal the superiority of heterogeneous catalysis over homogeneous catalysis. Homogeneous catalysts are unstable and undergo decomposition at higher temperature. The intrinsic catalytic activity or turn over frequency of the metal complex enhances significantly upon encapsulation. Heterogenization of complexes improves the properties such as selectivity, ease of catalyst separation, recyclability, thermal stability etc. in catalysis. Encapsulation in zeolite cages has received much attention in industrial field. This has prompted us to direct our studies to this area of interest.

A review on literature reveals the influence of heterocyclic ligands in complexes especially in catalytical field. Presence of heterocyclic ring as an
integral part of the ligand system can influence the nature and electronic properties of the metal ion in the complex. The purpose of the present work is to highlight the synthesis, characterization and some of the applications of Schiff base complexes as catalysts. Comparison of catalytic activity of the neat and encapsulated complexes may reveal the superiority of heterogeneous catalysis over homogeneous catalysis.
Chapter 2
Experimental Techniques

Details about the general reagents used, the preparation of ligands and the various analytical and physical methods employed in the characterisation of metal complexes are presented in this chapter.

2.1 Reagents used

Zeolite Y (Zeolite international, Netherlands), Sodium chloride (Merck), Salicylaldehyde (Merck) and 3-hydroxy benzaldehyde, 5- Aminouacil (Merck), 2-aminophenol (Merck), Nickel chloride and Cobalt chloride (Merck) were used in the present investigation. The solvents used such as DMF, Methanol, acetone, ether etc were of Merck. All materials used were of the highest purity available and were used without further purification. Phenol, hydrogen peroxide (30% aqueous solution) used for the catalytic studies were obtained from Merck.

2.2 Analytical Methods

A variety of techniques have been employed to characterize the synthesized complexes and to follow the course of catalytic reactions of the prepared compound.

2.2.1 CHN Analysis

Elemental analyses of the ligands and complexes were done by an Elementar model Vario EL III at SAIF, Sophisticated Test and Instrumentation
Centre, Kochi. These analytical data provide information about the structure of the ligands and help to quantify the organic ligands complexed to metal ions.

2.2.2. Chemical Analysis

The metal percentage present in the encapsulated complexes were determined by ICP-AES Spectrometer (Thermo Electron, IRIS Intrepid II XSP DUO) at SAIF, Sophisticated Test and Instrumentation Centre, Kochi.

Chemical analysis was done to determine the composition of zeolite samples. The given sample is digested with 5ml HNO₃ and made up to 100ml using HPLC grade water and analyzed with ICP-AES system. The dried zeolite sample was accurately weighed (X gram) and transferred to a beaker. Concentrated H₂SO₄ (40ml) was added and heated until SO₃ fumes were evolved. It was diluted with water and filtered through ashless filter paper. The residue was dried at 100°C in a platinum crucible, cooled and weighed (‘a’ g) Hydrofluoric acid was then added and evaporated and finally ignited to 1000°C (‘b’ g). The percentage of silica (SiO₂) was calculated using the equation.

\[ \%\text{SiO}_2 = \frac{(a-b)}{X} \times 100 \]

The degree of ion exchange in zeolite and unit cell formula are derived from Si /Al ratio. The Si /Al ratio of the zeolite complexes was compared with that of pure zeolite to make sure that the frame work was preserved in encapsulated complexes.

2.3 PHYSICO-CHEMICAL METHODS

2.3.1 Surface area analysis

Surface area of the samples were measured by multipoint BET method using a micromeritics Gemini 2360 surface area analyzer. Nitrogen gas was
used as the adsorbate at liquid nitrogen temperature. Surface area measurements have been carried out to know whether the encapsulation of guest molecules inside zeolite cages has occurred. A lower surface area of intra-zeolite complex as compared to metal exchanged zeolite indicates the filling of zeolite pores with complexes.

### 2.3.2 X-ray diffraction spectroscopy

X-ray diffraction pattern of the parent zeolite and zeolite encapsulated complex were recorded by Bruker AXSD8 Advance diffracometer. The evaluation of the spectra of host zeolite and zeolite complex was carried out to ensure that zeolite crystallinity is not affected by the encapsulation of the metal complex.

### 2.3.3 SEM

The morphology of the samples were examined using scanning electron microscopy at SAIF, Sophisticated Test and Instrumentation Centre, Kochi to determine whether there are any adsorbed materials or any morphological change occurred during the conditions of encapsulation. The samples were coated with a thin film of gold to prevent surface charging and to protect the zeolite material from thermal damage by electron beam.

### 2.3.4 Thermogravimetry

Thermogravimetric analyses were done on a Perkin Elmer. Diamond TG Analyser. Thermogravimetry is a technique in which a change in weight of substance is recorded as a function of temperature or time. TG curves of zeolite
sample were recorded in nitrogen atmosphere from ambient temperature up to 1200ºC at a heating rate of 10ºC /minute.

2.3.5 Infra red Spectra

IR Spectra of complexes in the region 4000- 500cm\(^{-1}\) were taken using Perkin Elmer Spectrum Two, FTIR spectrometer. FTIR provides valuable evidences for the formation of metal complexes in zeolite pores. The ligand molecules are coordinated to transition metal cations if different spectral pattern for them appear in the free and chelated state or if characteristic bands exhibit shift in frequency upon coordination.

2.4 Gas chromatography

The catalytic activity studies of the synthesized complexes in phenol oxidation reaction were performed with a Perkin Elmer CLARUS 580 Gas Chromatograph equipped with an FID detector. The various components of the reactants and products were separated by Elite 5 column.

2.5 Preparation of ligands

2.5.1 5- Aminouracil– 3-hydroxybenzaldehyde (AU3HB)

Accurately weighed 5- aminouracil was dissolved in ethanol with a few drops of glacial acetic acid by heating on a boiling water bath. It was boiled for about 10 minutes and treated with definite amount of 3- hydroxybenzaldehyde in ethanol. After continued refluxing for 2h the ligand get crystallized. Resulting solution was filtered, washed with water and dried over anhydrous calcium chloride.
2.5.2 5- Aminouracil- Salicylaldehyde (salau)

Accurately weighed 5- aminouracil was dissolved in ethanol with a few drops of glacial acetic acid by heating on a boiling water bath. It was boiled for about 10 minutes. A definite amount of salicylaldehyde was dissolved in ethanol. This was added to round bottom flask containing 5- aminouracil and ethanol. After continued refluxing for 2h the ligand get crystallized. Resulting solution was filtered, washed with water and dried over anhydrous calcium chloride.

2.5.3 Salicylaldehyde– o-aminophenol (salap)

Salap is prepared by dissolving accurately weighed o-aminophenol in methanol under reflux. It was boiled for about 10 minutes. A definite amount of salicylaldehyde was dissolved in methanol. This was added to round bottom flask containing o-aminophenol and ethanol. The volume of the solution was reduced by distillation of the solvent. The orange colored solid formed. It was filtered, washed with methanol and ether. Then it was dried under vacuum over phosphorous pentoxide.

2.5.4 3- Hydroxybenzaldehyde-o-aminophenol (HBAP)

Dissolve accurately weighed o-aminophenol in methanol under reflux. It was boiled for about 10 minutes. A definite amount of 3-Hydroxybenzaldehyde was dissolved in methanol. This was added to round bottom flask containing o-aminophenol and ethanol. The volume of the solution was reduced by distillation of the solvent. After continued refluxing the ligand get crystallized. Resulting solution was filtered, washed with water and dried over anhydrous calcium chloride.
2.6 Synthesis of Simple complexes.

Simple complexes of Iron, Cobalt and nickel were prepared with above Schiff bases.

2.6.1 Synthesis of Cobalt complexes with AU3HB, salau, salap, HBAP ligands

Cobalt chloride dissolved in ethanol were added to the refluxed solution of AU3HB in DMF in 1:2 ratio. It was then refluxed for 6 h. The complex solution was concentrated by evaporation of the solvent and cooled. The precipitated complex was filtered and washed several times with ethanol. The complex was dried over anhydrous calcium chloride.

The same methodology was followed for the synthesis of other simple complexes of cobalt with Schiff bases salau, salap, HBAP.

2.6.2 Synthesis of Nickel complexes with AU3HB, salau, salap, HBAP ligands

Nickel chloride dissolved in ethanol were added to the refluxed solution of AU3HB in ethanol in 1:2 ratio. The mixture was refluxed for 6 h. The complex solution was concentrated by evaporation of the solvent and cooled. The precipitated complex was filtered and washed several times with ethanol. The complex was dried over anhydrous calcium chloride.

The same methodology was followed for the synthesis of other simple complexes of nickel with Schiff bases salau, salap, HBAP.

2.6.3 Synthesis of Iron complexes with AU3HB, salau, salap, HBAP ligands

Ferric chloride dissolved in ethanol were added to the refluxed solution of AU3HB in ethanol in 1:2 ratio. The solution was refluxed for 6 h.
The complex solution was concentrated by evaporation of the solvent and cooled. The precipitated complex was filtered and washed several times with ethanol. The complex was dried over anhydrous calcium chloride.

Simple complexes of nickel with Schiff bases salau, salap, HBAP were also prepared by the same methodology.

2.7 MODIFICATION OF ZEOLITE – Y

2.7.1 Preparation of Sodium exchanged Zeolite (NaY)

Zeolite –Y (5.0g) was stirred with a solution of NaCl (0.1M, 500ml) for 24 h using magnetic stirrer. This is to convert any other ions if present in the zeolite into Na⁺ ions. It was then filtered and made chloride free by washing with distilled water. The NaY formed was dried at 100ºC for 2h.

2.7.2 Preparation of Metal exchanged Zeolite (MY)

The metal salt (cobalt chloride, Nickel chloride, Ferric Chloride) was accurately weighed and dissolved in 500ml of distilled water. To this solution 5g of sodium exchanged zeolite was added and is stirred at 70ºC for 4h using magnetic stirrer. Low concentration of metal salt solution was used because in higher concentration, dealumination occurs. The slurry was filtered using No.1 filter paper. It was washed with deionized water to make it free from anions. It was then dried at 130ºc for 1h and then 450ºc for 4h.

2.8 Synthesis of Zeolite encapsulated metal complexes of iron, cobalt and nickel with AU3HB, salau, salap, HBAP Schiff base ligands.

The metal exchanged zeolite was mixed with each of the above ligands and is dried at 200ºc for 4h in muffle furnace. The ligand penetrates through the
pores of zeolite and complexes with the metal ions already present within the zeolite. The size of the complexed product is very large so it is very difficult to pass through the aperture of the supercage. So it will be retained inside the cages. The resultant mass was covered with No.1 filter paper. This was soxhlet extracted with methanol until the extracting solvent became colourless. The uncomplexed metal ions in the zeolite and ionisable portions of the ligand were removed by ion exchanging with NaCl solution for 24h. It was filtered. It was washed with deionised water to make it free from chloride ions. Finally it was dried at 100ºc for 2h and stored in vacuum over anhydrous calcium chloride.

2.9 Catalytic hydroxylation of phenol

2.9.1 Procedure

Hydroxylation of phenol was carried out in a thermostated reactor of 100ml volume fitted with a magnetic stirrer. The reaction was equipped with a reflux condenser. For high temperature reactions temperature controlled oil-bath was used. For the reaction phenol (1ml), H₂O₂ (5ml), and H₂O (5ml) were taken. Reaction was initiated by adding 40mg catalyst. Reactions were done at room temperature and at 80ºC. Solution from the reaction vessel was withdrawn at definite intervals of time 1h, 2h, 3h,……. The reaction mixture was cooled to room temperature and the products were analyzed.

2.9.2 Analysis of products

Products of hydroxylation reaction were analyzed in a gas chromatograph equipped with a flame ionization detector using Elite 5 column.

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Phenol hydroxylation was carried out in the absence of the catalyst. It was found that no product was formed even after 6h.
Chapter 3
Results and Discussion

3.1 Elemental Analysis

The analytical data suggest all the ligands act as bidentate and coordinate through azomethine nitrogen and phenolic oxygen of aldehyde moiety. The complexes may be assigned to have empirical formula ML₂(H₂O)₂.

Elemental analyses reveal a Si/Al ratio of 2.6 for NaY that corresponds to a unit cell formula Na₅₄(AlO₂)₅₄(SiO₂)₁₃₈.nH₂O for NaY[63]. Almost constant value of Si/Al ratio after the metal exchange and formation of complexes confirms that zeolite frame work retains its crystal structure[64]. This also indicates that dealumination did not take place during metal exchange and encapsulation. Ion exchange take place according to the equation

$$\text{Na}_5\text{Y} + x\text{M}^{3+} \rightarrow M_x\text{Na}_{54-3x}\text{Y} + 3x\text{Na}^+$$

Where x represents the fraction of M³⁺ ions exchanged with Na⁺ in the zeolite [65]. Elemental analyses of the metal exchanged zeolite CoY indicate the unit cell formula to be Na₄₀.₃Co₆.₈₅(AlO₂)₅₄(SiO₂)₁₃₈.nH₂O. The degree of ion exchange of cobalt is calculated from the percentage of cobalt in the sample and found to be 16.88. Further the presence of carbon, hydrogen and nitrogen suggest the formation of metal complexes in the zeolite cages. Unit cell of FeY was calculated to be Na₄₈.₈Fe₂.₄(AlO₂)₅₄(SiO₂)₁₃₈.nH₂O and that of NiY Na₂₄Ni₁₅(AlO₂)₅₄(SiO₂)₁₃₈ from metal analysis. The degree of ion exchange in FeY is 12.88 and in NiY is 53.
Table 1. Analytical data of ligands and complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>% C</th>
<th>%H</th>
<th>%N</th>
<th>%Metal</th>
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<td>AU3HB</td>
<td>56.7</td>
<td>3.5</td>
<td>22.03</td>
<td>-</td>
</tr>
<tr>
<td>Salau</td>
<td>57.08</td>
<td>3.8</td>
<td>22.5</td>
<td>-</td>
</tr>
<tr>
<td>Salap</td>
<td>73.1</td>
<td>5.1</td>
<td>6.3</td>
<td>-</td>
</tr>
<tr>
<td>HBAP</td>
<td>73</td>
<td>4.9</td>
<td>6.4</td>
<td>-</td>
</tr>
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<td>CoAU3HB</td>
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<td>3.1</td>
<td>15.9</td>
<td>11.1</td>
</tr>
<tr>
<td>NiAU3HB</td>
<td>50.2</td>
<td>2.9</td>
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<td>11.3</td>
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<td>%N</td>
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<td>2.543</td>
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</table>
3.2 **Surface area**

Surface area of metal exchanged zeolite is smaller than sodium exchanged zeolite. This can be attributed to the large size of metal compared to sodium. Encapsulation resulted in decrease in surface area due to the large size of the complex encapsulating in the cage. This results in filling of the pores of zeolite thereby reducing surface area.

3.3 **X-ray diffraction studies**

The powder X-ray diffraction patterns of NaY, FeY, CoY, NiY and encapsulated complexes exhibit similar pattern, though slight change in the intensity of the bands were noticed. These observations indicate that the framework of the zeolite has not undergone any significant structural change on complexation. This suggests that the crystallinity of the zeolite Y is preserved during encapsulation. No new peaks could be detected in zeolite encapsulated complexes probably due to poor loading of the complex in zeolite framework.

3.4 **SEM analysis**

The scanning electron micrographs (SEM) of the complexes before and after encapsulation indicate that surface species are completely removed by soxhlet extraction.
Scanning Electron Micrographs of (i) before and (ii) after soxhlet extraction

### 3.5 Infrared Spectra

The FTIR spectra bands of the ligands, simple and supported complexes were recorded in the region 400-4000 cm\(^{-1}\). The infrared spectra of all the ligands showed a broad band in the region 3390-3480 cm\(^{-1}\) which might be due to \(\nu_{OH}\). The observed low value of this band is due to intra molecular hydrogen bonding between hydrogen of OH and azomethine nitrogen. In all the ligands band around 1630 cm\(^{-1}\) were assigned to \(\nu_{C=N}\) which was shifted to lower frequency after complexation indicates coordination of azomethine nitrogen with the metal. The around 1710 cm\(^{-1}\) corresponding to \(\nu_{C=O}\) in the ligand salau, AU3HB remains unshifted after complexation indicates nonparticipation of carbonyl group of aminouracil moiety in coordination. A strong band at 1135 cm\(^{-1}\) in the free Schiff bases have been assigned to phenolic C-O
stretching. On complexation the band is shifted to higher frequency indicating coordination through phenolic oxygen.

A broad and medium intensity band around 3400 cm\(^{-1}\) in all complexes is due to \(\nu_{\text{OH}}\) of lattice held or coordinated water molecule. The presence of coordinated water in the complexes is indicated by the infrared band around 855 cm\(^{-1}\).

The infrared frequencies of metal exchanged zeolite and the parent zeolite are of almost the same value as reported in earlier studies. This indicates the nondestruction of the zeolite frame work by the metal exchange. The band around 1630 cm\(^{-1}\) in the ligand are shifted to lower frequencies in all the complexes which confirms complexation at nitrogen of the azomethine group. The stretching vibrations of water molecules present in the zeolite lattice can be seen around 3400 cm\(^{-1}\). In the IR spectra of the free ligand, band occurs in around 1140 cm\(^{-1}\) due to \(\nu_{\text{C-O}}\) of phenolic group. However this is absent in encapsulated complex. This might be due to the masking by the broad zeolite band around 1000 cm\(^{-1}\) which is not seen in the corresponding ligand. Hence it can be assigned to the zeolite framework vibration. The peak around 1020-1030 cm\(^{-1}\) and around 580 cm\(^{-1}\) may be due to zeolite.

### 3.6 Thermogravimetric analysis

The thermal decomposition of the zeolite encapsulated complexes of Fe, Co and Ni occurs in two major steps. An endothermic weight loss of about 16-18\% is observed in the temperature range 30-150°C in all the complexes. Such a weight loss is observed in the case of metal exchanged zeolite also. Hence this might be due to the removal of intrazeolite water. The second step of exothermic weight loss occurs in a single step and starts immediately after the first step and continues till 800°C in all complexes. A weight loss of about 10\% due to the slow decomposition of the metal complex is observed in this wide
temperature range. This type of weight loss is not envisaged in the thermal decomposition curve of metal exchanged zeolite which provides additional evidence of the formation of metal complex in the zeolite matrix. The variation in the thermal decomposition pattern exhibited by different complexes is indicative of the formation of the metal complexes. The small percentage of weight loss indicates the insertion of only small amount of metal complexes in the cavity of the zeolite. This is in agreement with the observed low percentage of metal content in encapsulated complexes. The zeolite framework is to be destroyed only above 800ºC in all complexes.

3.7 Catalytic studies

Neat and zeolite encapsulated complexes of Fe, Co and Ni with the Schiff bases derived by condensing 5-aminouracil with a) 3-hydroxy benzaldehyde, b) salicylaldehyde and o-aminophenol. Complexes were screened towards phenol hydroxylation reaction. The reaction was monitored at different time intervals at room temperature and at 80ºC. The percentage conversion obtained with various catalysts is given in Table 3. The only product formed was hydroquinone.

In the presence of simple complexes more than 50% conversion of phenol to hydroquinone take place in one hour. At higher temperature higher percentage of hydroquinone was formed initially. But in the third hour a tarry product was formed. Hence it is not advisable to prolong the reaction if conducted at higher temperature.
Table 3. Effect of Temperature and Time on Oxidation of Phenol in the presence of Simple Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>1h %HQ</th>
<th>2h %HQ</th>
<th>3h %HQ</th>
<th>4h %HQ</th>
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Table 4. Effect of Temperature and Time on Oxidation of Phenol in the presence of Zeolite encapsulated complex

<table>
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<th>3h %HQ</th>
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Fig.I Percentage of Hydroquinone formed in the presence of simple and encapsulated complexes of cobalt after 1h

![Graph showing percentage of Hydroquinone formed in the presence of simple and encapsulated complexes of cobalt after 1h.]

Fig.II Percentage of Hydroquinone formed in the presence of simple and encapsulated complexes of cobalt after 3h

![Graph showing percentage of Hydroquinone formed in the presence of simple and encapsulated complexes of cobalt after 3h.]
In presence of zeolite encapsulated complexes oxidation of phenol follows a similar trend as observed in the case of analogous simple complex. However higher percentage of hydroquinone was formed in each case. Increase in temperature in this case did not affect the percentage conversion much, although a slight increase in the yield of the product was noted. However the stability of the catalyst was increased at higher temperature due to encapsulation.

3.8 Conclusion

Of the two types of complexes simple and encapsulated, zeolite encapsulated complexes were found to be more active towards hydroxylation reaction of phenol. This might be due to the shape selectivity of the zeolite pore and vacant coordination sites of the metal ion inside the pore. Optimum conditions for good yield of product could be selected as room temperature up to 4 h. At higher temperature the reaction products soon converted in to tarry product in all cases. However it was noted that encapsulated complexes withstand high temperature. Also on analyzing the facts it can be concluded that encapsulated complexes are more active as compared to simple complexes.
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