

1.1 INTRODUCTION

Porous materials have been center of attention and under surveillance since from last few decades because of their many-fold applications in the realm of material science. Zeolites, one of most well-known members of porous materials, are hydrated aluminosilicate minerals, crystalline and microporous in nature and are made up of interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4) units. Open, cage-like framework with channels, windows and nano-scale level cages of specific and regular size is the most interesting feature about zeolite.¹⁻³ Zeolites have huge applications in separation, molecule recognition and nano-scales reactors and in catalysis along with many others.^{4,5} The zeolites are used as catalysts in various gas or solution phase reactions and employed to improve catalytic processes for the production of the fine chemicals. Towards the intend of accomplishing specific targets, zeolites with precise architecture emerge as very promising materials for the encapsulation of variety of transition metal complexes, organometallics, organic dyes and polymer within their voids. These host-guest hybrid systems facilitate catalysis more efficiently as they are equipped with high thermal stability, strong host-guest interactions and size and shape selectivity. Size and shape selectivity is another distinctive feature of the crystalline microporous materials which has a significant footprint in catalytic performances of the material. Encapsulation of metal complex inside the supercage of zeolite, is a prominent route to tuning the activity of metal complex as the additional features like robustness and stereochemistry of zeolite framework are appended to the system. The topology of the cavities and the steric and electrostatic constraints of the zeolitic walls can modify the structure of the guest molecules substantially and consequently, these outcomes can create significant changes in magnetic, electronic, and redox and hence, catalytic properties of the encapsulated guest molecules.

Some of these hybrid systems are well-known mimics of biological systems and therefore referred as “zeozymes” because these hybrid systems act as prototypes of enzyme active centers where the zeolite framework imitates to a rigid protein mantle.^{6,7} The zeolite encapsulated iron phthalocyanine complexes are established as efficient catalysts and mimics the oxidation activity of the cytochrome P450 enzyme.⁸

Reusability of these encapsulated systems is another significant advantage which also makes them an economically proficient catalysts in place of many transition metal complexes as they are expensive and non-recoverable when they are employed as homogeneous catalysts. However, once encapsulated in zeolite these metal complex can be recyclable for several times without compromising on reactivity and manifest better catalytic activity and selectivity and high thermal stability in comparison to the

homogeneous analogues. Zeolite framework actually provides a controlled environment to the guest metal complex which is actually instrumental for the enhancement of reactivity of system.⁹⁻¹²

Another interesting fact is established about the alkali metal cations which are present in zeolite framework. These exchangeable charge compensating alkali metal cations manage to enhance the donor strength of the zeolite framework and the strength of the framework increases with increasing electro-positivity of the alkali cations.¹³ Physicochemical properties such as electric field and electrostatic potential within the supercage of zeolite framework, spin-orbit parameter, and space availability for guest molecules inside the supercage are controlled by these exchangeable charge compensating alkali metal cations.^{14, 15}

The walls of zeolite framework provide space constraint to the guest metal complex and the topology of host framework induces visible changes in the spectroscopic, redox and magnetic behavior of the guest metal complex¹⁶⁻¹⁹. Consequently, encapsulated metal complex shows the modified reactivity, often quite different from its homogeneous form. Many such encapsulated metal complexes have already been established as efficient catalysts for several oxidation reactions.^{20, 21}

The motif of this thesis is to address the correlation between the modified catalytic activity and tunable electronic environment of metal complexes. This thesis therefore deals with the synthesis, characterization and catalytic studies of square-planar Cu (II), Co (II), Pd (II) and Ni (II) Schiff-base complexes where these metal complexes are synthesized in free as well as in zeolite-Y encapsulated-state. Few M (II) Schiff-base complexes are selected such that they have molecular dimension or end-to-end dimension comparable to the dimension of supercage of zeolite-Y. Once synthesized, the guest molecule is unable to leak out from the host cavity through the channels. Therefore, these encapsulated-state hybrid systems are referred as *ship-in-a-bottle* complexes. In the current study, we have synthesized M (II) Schiff-base complexes with a range of molecular dimensions by attaching different substituents on the Schiff-base ligand moiety and employing different metals. These systems are well characterized by using various spectroscopic techniques like XRD (X-ray diffraction), SEM-EDX (scanning electron microscopy with energy dispersive X-ray analysis), BET (Brunauer-Emmett-Teller) surface area analyzer, thermal analysis, XPS (X-ray photo electron spectroscopy), IR (Infrared spectroscopy), UV-Vis (Ultraviolet-visible) studies, magnetic susceptibility measurements and theoretical studies. These synthesized hybrid systems are then employed as catalysts for oxidation, coupling and dye degradation reactions. M(II) Schiff-base complexes are synthesized in free-state as well as in encapsulated-states. Typical method to encapsulate a metal Schiff-base complex inside the

cavities of zeolite complex is achieved via *flexible ligand synthesis method* where transition metal (Cu, Co, Pd and Ni) and Schiff-base ligands with general formula: *N,N'*-bis(salicylidene)-1,2-phenylenediamine (L1), *N,N'*-bis(5-hydroxysalicylidene)-1,2-phenylenediamine (L2), *N,N'*-bis(5-bromosalicylidene)-1,2-phenylenediamine (L3), *N,N'*-bis(5-methylsalicylidene)-1,2-phenylenediamine (L4), *N,N'*-bis(5-methoxysalicylidene)-1,2-phenylenediamine (L5), *N,N'*-bis(5-nitrosalicylidene)-1,2-phenylenediamine (L6), *N,N'*-bis(salicylidene)-1,3-phenylenediamine (L1'), *N,N'*-bis(5-hydroxysalicylidene)-1,3-phenylenediamine (L2'), *N,N'*-bis(5-bromosalicylidene)-1,3-phenylenediamine (L3'), *N,N'*-bis(5-methylsalicylidene)-1,3-phenylenediamine (L4'), *N,N'*-bis(5-methoxysalicylidene)-1,3-phenylenediamine (L5') and *N,N'*-bis(5-nitrosalicylidene)-1,3-phenylenediamine (L6') are used (presented in Figure 1.14). The aspects of the present study are discussed as follows.

- ❖ **Transition metal Schiff-base complexes as catalysts**
- ❖ **Zeolites: Structure and composition**
- ❖ **Heterogenization of transition metal complexes**
- ❖ **Zeolite encapsulated metal complexes as heterogeneous catalysts**
- ❖ **Zeolite encapsulated metal complexes: structural aspects**

1.1.1 Transition metal Schiff-base complexes as catalysts

Transition metal Schiff-base complexes have been generally explored for their numerous industrial and biological applications.²² These complexes are extensively studied because of their therapeutic activity such as antifungal, antibacterial, anticancer and herbicidal activities.

Metal Schiff-base complexes mostly show good catalytic activity for various reactions such as polymerization, oxidation, decomposition of H₂O₂, carbonylation, coupling reactions, and Lewis acid assisted organic transformations.

The most prominent field of application of the metal Schiff-base complexes is catalysis. Co(II), Cu(II), Zn(II) and Pd(II) Schiff-base complexes are effectively employed as catalysts for the oxidation of sulfides into corresponding sulfones in presence of hydrogen peroxide. These catalytic reactions are carried out without solvent employing a green sustainable path in presence of all the metal complexes catalysts.²³ First transition metals such as Co(II), Cu(II), Fe(II), Mn(II), Ni(II) and Zn(II) complexes of dithiocarbamate Schiff-base ligand are explored as catalysts for the oxidation of cyclohexane using H₂O₂ as oxidant. These catalysts show ample selectivity for cyclohexanone as compared to

cyclohexanol.²⁴ Copper(II) Schiff-base complexes has been employed for the oxidation of alkenes, alkanes and aromatic alcohols at room temperature in presence of H₂O₂ as oxidant.²⁵

Seyedi and coworkers reported the novel Co(II) complexes of Schiff-bases utilized for the oxidation of alcohols to the corresponding aldehyde and ketones in presence of molecular oxygen and catalytic reactions successfully proceed without further oxidation of aldehydes to their respective acids in aqueous medium. This catalytic reaction manifests many advantages such as easy handling, broad substrate applicability, good yields achieved in short reaction times. Here, Schiff-bases are derived from the amino acids and these catalytic reactions are carried out in aqueous medium and in presence of molecular oxygen which makes these catalysts ecofriendly.²⁶ Begum's group also reported the synthesis of a novel series of Cu(II), Ni(II), Zn(II), Co(II), and Cd(II) Schiff-base complexes. These complexes are proven to be efficient catalysts for the oxidation of benzyl alcohol to benzaldehyde and more significantly, zinc, copper and cadmium complexes have potent antitumor efficacy.²⁷ Heshmatpour *et al.* have synthesized copper(II) Schiff-base complexes, where Schiff-bases are derived by the reaction of 2,2'-dimethyl-propanediamine with bis(2-hydroxy-propionophenone) and bis(5-bromosalicylaldehyde). These complexes show good catalytic activity towards the oxidation of styrene and cyclooctene in presence of *tert*-butyl hydroperoxide as the oxidant.²⁸

The catalytic activity of these metal complexes is further examined whether these complexes have prospect to act as efficient catalysts for the chemical fixation of CO₂ into the respective cyclic carbonates by epoxides.²⁹ Zn(II) Schiff-base complex is found as the most active catalyst for the chemical fixation of CO₂. With the investigations of different parameters by using this metal complex as a catalyst and after comparing the catalytic activity of all these complexes, they have concluded that the azo group has a positive effect on the activity.

Zhou *et al.* synthesized a series of palladium Schiff-base complexes with or without phenolic hydroxyl groups. These palladium complexes are noted as efficient catalysts for the Suzuki–Miyaura coupling reactions of aryl iodides, aryl bromides and activated aryl chlorides and hence a simple and low-cost methodology for Suzuki–Miyaura reaction in presence of aqueous ethanol medium has been developed. They have highlighted the influence of catalytic activity while introducing phenolic hydroxyl and pyridine groups to the Schiff-base ligand moiety.³⁰

Homogeneous catalysts are generally highly active as well as selective, but a main issue related to these catalysts lies into the difficulty of their separation from the reaction mixture, and hence their recyclability. The most effective way to resolve this problem is heterogenization of these homogeneous catalysts. Therefore, during recent years several strategies have been employed to design a

novel heterogeneous catalysts where these above mentioned homogeneous catalysts can be embedded on suitable mesoporous and microporous hosts.

1.1.2 Zeolites: Structure and composition

Zeolites have unique three dimensional (3D) architecture and is made up of SiO_4^{4-} and AlO_4^{5-} tetrahedral units (shown in Figure 1.1). This aluminosilicate framework is crystalline in nature and characterized as microporous material or inorganic polymer. The SiO_4^{4-} and AlO_4^{5-} tetrahedral units are basic building blocks of the framework and these units are connected to each other via a single oxygen atom shared by both the blocks as a corner. Extra-framework ions such as lithium, sodium, potassium and ammonium etc. are found in the zeolite framework to retain the charge neutrality of the material. The silicon atom is substituted by isomorphous aluminium atoms, which is registered as the distinct property of these materials and is represented by the Si/Al ratio. Generally, zeolites follow Löwenstein rule and according to the rule, each aluminium atom should be surrounded by four silicon tetrahedral units. In general, these tetrahedral units are represented as TO_4 where T stands for the tetrahedral units. These tetrahedral units are interlinked and to form truncated octahedron known as sodalite or β -cages (shown in Figure 1.1).

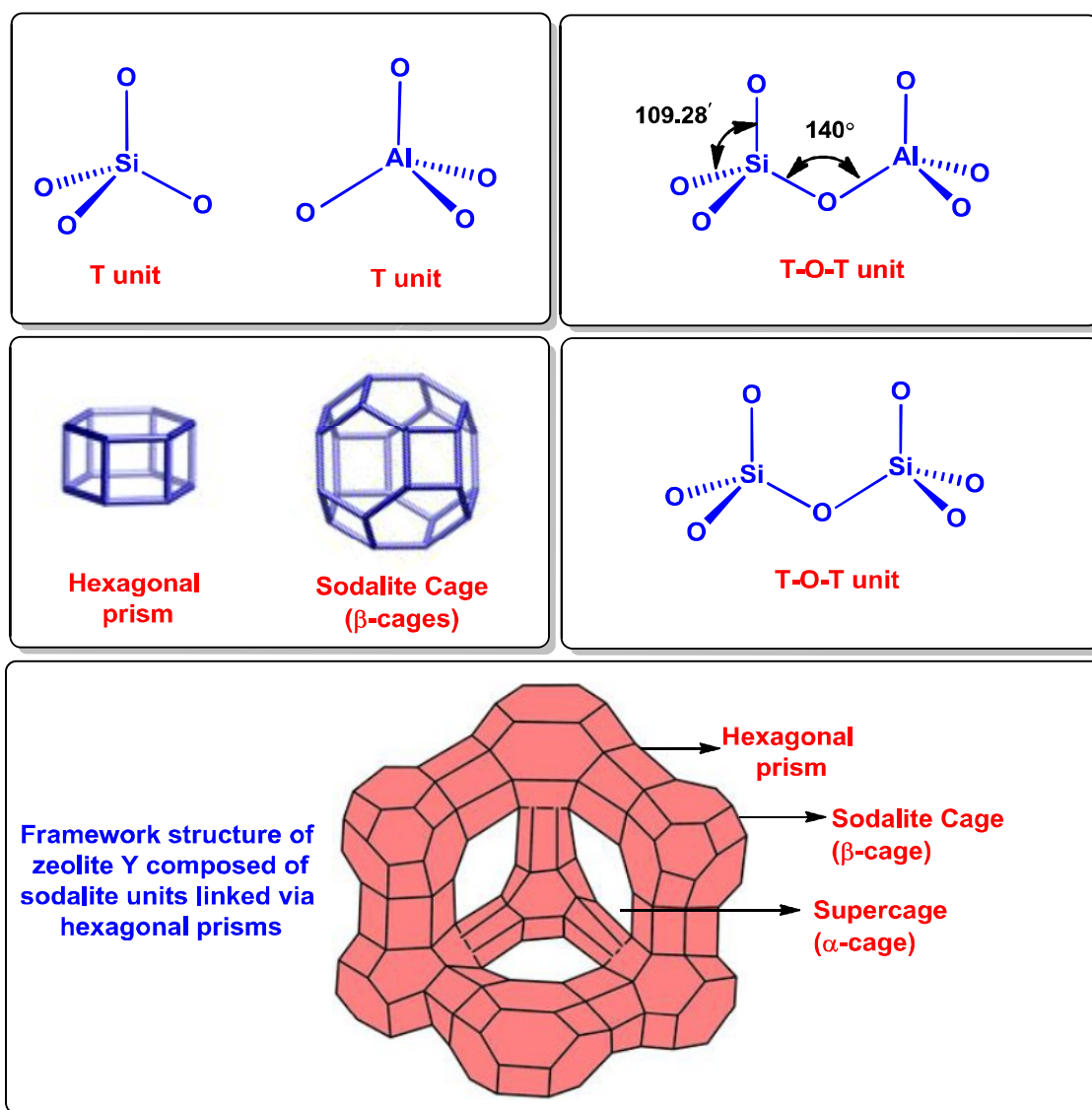


Figure 1.1: Schematic representation of different structural parts of Zeolite-Y.

These sodalite cages are connected through a double hexagonal prism (six-membered ring) to form a larger cage and is known as super cage or α -cage (shown in Figure 1.2). The structural and chemical aspects of zeolite are governed by the tetrahedral units and their members like oxygen and Si/Al ratio. Therefore, these factors define the zeolite materials with ultra-large, large, medium and small cages.³¹ The secondary building units (SBU) are comprised of the connecting of 16 basic building block units (BBU) and these secondary buildings units are linked up to form the hollow three dimensional (3D) network.³² These include condensed octahedral β cage made by 4 and 6 rings and interconnecting 8

rings compose an α cage. Zeolite Y, as quite an important member of the zeolite family, belongs to this class of materials and has the faujasite (FAU) structure.³²

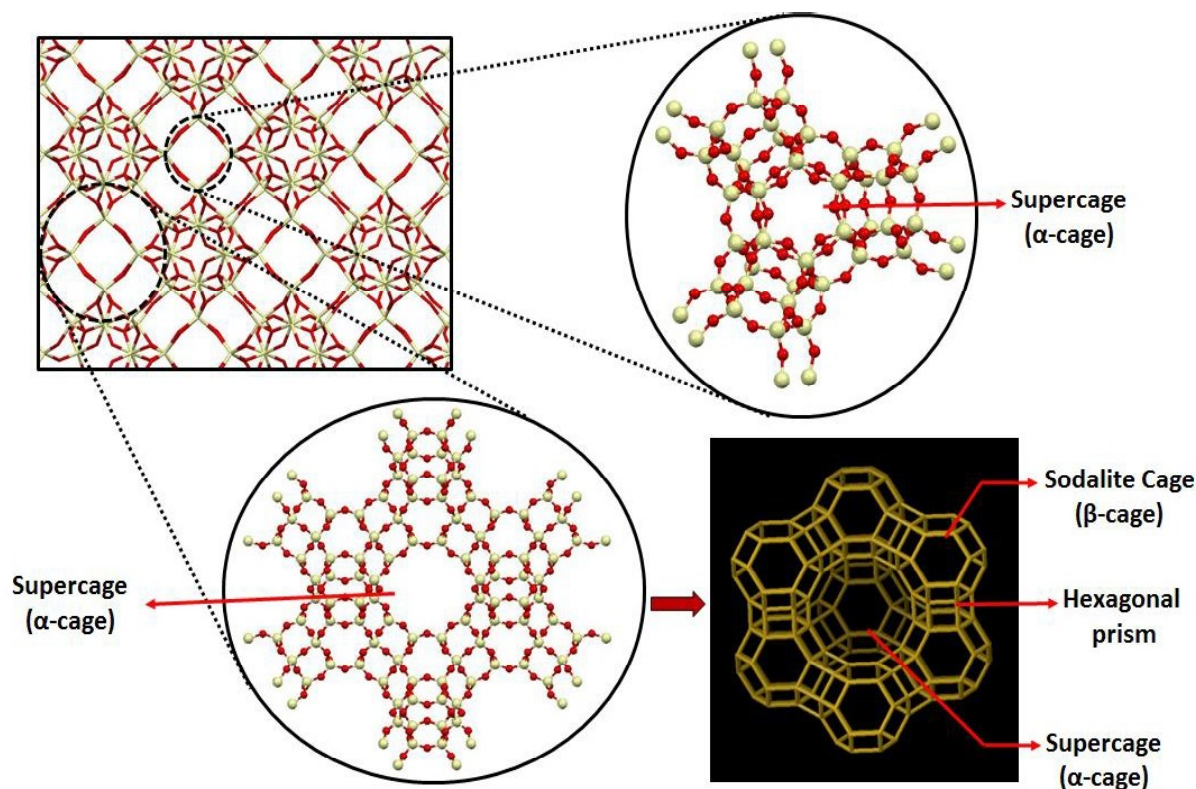


Figure 1.2: Framework of Zeolite –Y showing sodalite cages and supercages.

1.1.3 Heterogenization of transition metal complexes

One of the most popular techniques of heterogenization of the transition metal complexes is *via* immobilizing, grafting, anchoring or encapsulating them in an inert solid like organic or inorganic polymeric support. With regular size and shape of windows, channels and cavities, microporous aluminosilicate Zeolite-Y satisfies all conditions of inert, stable host. The precise architecture of the framework allows diffusion of the molecules inside the cavities of zeolite-Y. Such type of distinctive structural characteristic of the material makes it a suitable host material for the encapsulation of transition metal complexes. Large transition metal complexes are synthesized within the cavities of zeolites and are termed as zeolite encapsulated metal complexes (ZEMC). Once synthesized, the structural rigidity does not allow the complex to escape from the cavity and hence, sometimes more suitably these host-guest systems are known as ‘ship-in-the-bottle’ complexes.

Zeolite encapsulated metal complexes demonstrates many advantages over the homo and traditional heterogeneous catalysts as these systems deliver many openings to design and develop catalytic processes for various reactions such as hydrogenation, oxidation, alkylation, cyclization, acylation and isomerization. Bedioui has suggested three general methods for the preparation of zeolite encapsulated metal complexes, as listed below.

- ❖ **Flexible ligand method**
- ❖ **Template synthesis method**
- ❖ **Zeolite synthesis method**

1.1.3.1 Flexible ligand method

Flexible ligand method is used for the synthesis of a specific type of zeolite encapsulated systems, where the ligand moiety has structural flexibility such as Schiff base ligands.^{21, 33} In this approach, transition metal ions are introduced within the zeolite framework by using an ion-exchange reaction. These mobile alkali metal ions such as lithium, sodium and potassium etc. present to balancing charges of the framework can easily be exchanged by desired transition metal ions. Ion exchange reaction is an important fundamental step for the synthesis of zeolite encapsulated metal complexes via the ‘flexible ligand method’ and ‘template synthesis method’. For the ion exchange reaction, parent zeolite is allowed to react with the desired transition metal salt solution to get the targeted loading level of metal ions in the zeolite framework. The reaction proceeds at room temperature for 24 h and then the slurry is filtered and washed repeatedly and desiccated for 1-2 days at 150 °C. In flexible ligand method, a flexible ligand is then allowed to diffuse through the ion-exchanged zeolite pores by the heating of reaction mixture at high temperature for 24-48 h. The flexible ligand, on encountering the metal ion, within the supercage of zeolites, reacts and forms the encapsulated complex (shown in Figure 1.3). The synthesized encapsulated metal complex is washed repeatedly by using Soxhlet extraction with various solvents such as acetone, acetonitrile, methanol, and diethyl ether to remove the excess unreacted ligand and surface adsorbed metal complexes.^{33, 34} The final compound is dried in a muffle furnace for 10-12 h at 150 °C and then is further reacted with sodium chloride solution for 12 h at room temperature to remove the unreacted transition metal ions. Then, reaction mixture is filtered and washed with distilled water until the filtrate shows negative test for chloride ions. The molecular dimension of the complex is when comparable with the diameter of the nearly spherical supercages of zeolite, then the encapsulated complex is eventually entrapped within the supercage of

the host as it is too large to escape through the windows. This approach is appropriate for the synthesis of encapsulated metal salen complexes, since the salen ligand has the desired flexibility. The thermal stability of the ligand indeed plays a key role in this method as the ligand should not be decomposed at the reaction temperature. The flexible salen ligand diffuses through the windows and enters within the supercage. Diffusion possibly becomes easier because of the free rotation around the carbon-carbon and carbon-nitrogen sigma bond connecting the two salicylidene moieties of the salen ligand. However, once the metal complex formed within the supercage, the ligand loses its flexibility and forms square planar complex and entrapped. This method is first reported by Herron for the synthesis of zeolite encapsulated cobalt salen complexes.³⁵ Later, this procedure has been employed for the encapsulation of various transition metal complexes such as Schiff-base complexes of cobalt,³⁵ nickel,³⁶ copper,³⁷ iron,³⁸ manganese,³⁴ palladium,³⁹ vanadium,³⁷ and zinc³⁶ in zeolite Y.

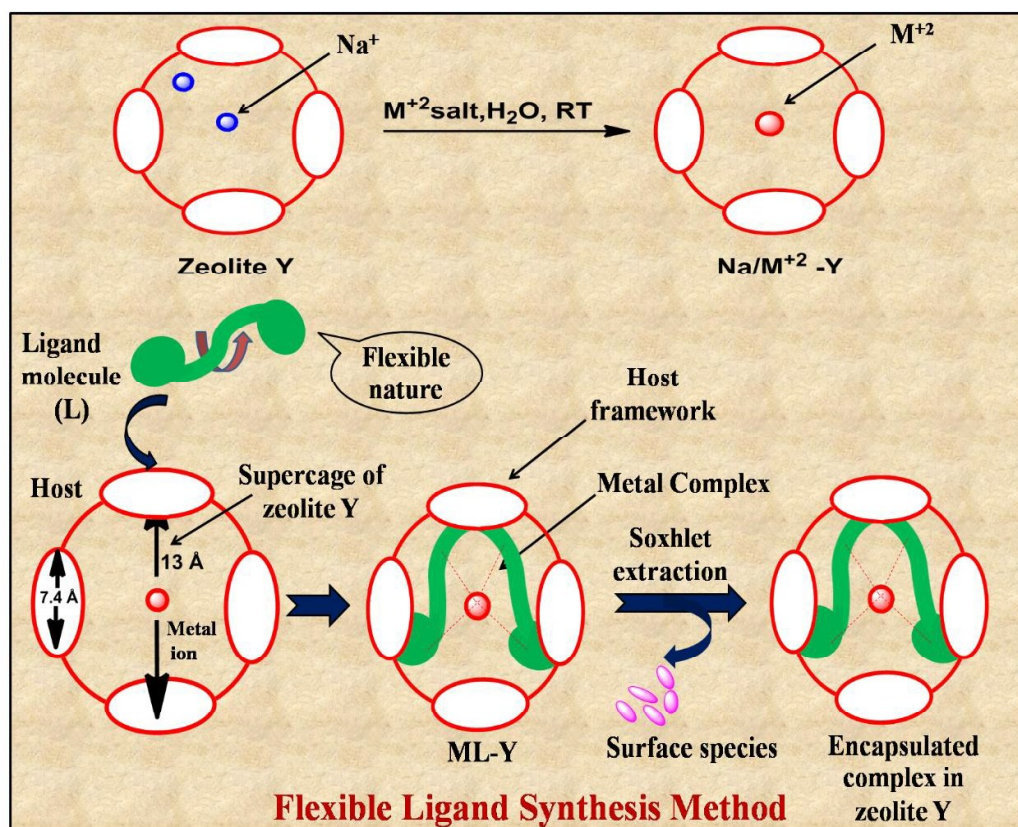


Figure 1.3: Synthesis of M/Na-Zeolite -Y and encapsulation of 'ship-in-a-bottle' metal complex in void of zeolite via 'flexible ligand method'.

1.1.3.2 Template synthesis method

This method is mainly useful when the molecular dimension of the ligand is larger than the diameter of the windows connected to the supercage. Therefore, diffusion of the ligand through the windows is not feasible. Under such condition, the precursor molecules or the building blocks of ligand molecule are allowed to diffuse through and react within the supercages of metal exchanged zeolite. In this approach, '*in situ*' complex formation takes place to finally attain the rigid 'ship-in-a-bottle' complex. This method is extensively used for the synthesis of zeolite encapsulated transition metal complexes of bipyridyl, phthalocyanine and porphyrin ligand systems (shown in Figure 1.4). For example, to synthesize tris(bipyridyl) metal complex within the supercage of zeolite-Y, bipyridine is allowed to diffuse through the windows of zeolite as a precursor molecules. Synthesis of zeolite encapsulated M(II)-tris(bipyridyl) complex was first reported by Mizuno and Lunsford.⁴⁰ In case of phthalocyanine ligand, the precursor molecule is 1,2 dicyanobenzene and these precursor molecules are allowed to diffuse through and assembled together to form ligand and subsequently the metal phthalocyanine complex. The final step includes reduction of the phthalocyanine precursor. For this reduction zeolitic water molecules play an important role providing the electron. Therefore, to complete the synthesis of phthalocyanine metal complex within the cavities of zeolite, complete dehydration of zeolite framework essentially requires to be avoided. This method has been used to prepare different encapsulated phthalocyanine complexes e.g., cobalt,^{18,41,42} nickel,⁴¹ copper,⁴³ iron,⁴⁴ ruthenium⁴⁵ and rhodium⁴⁶ phthalocyanines inside zeolite-Y.

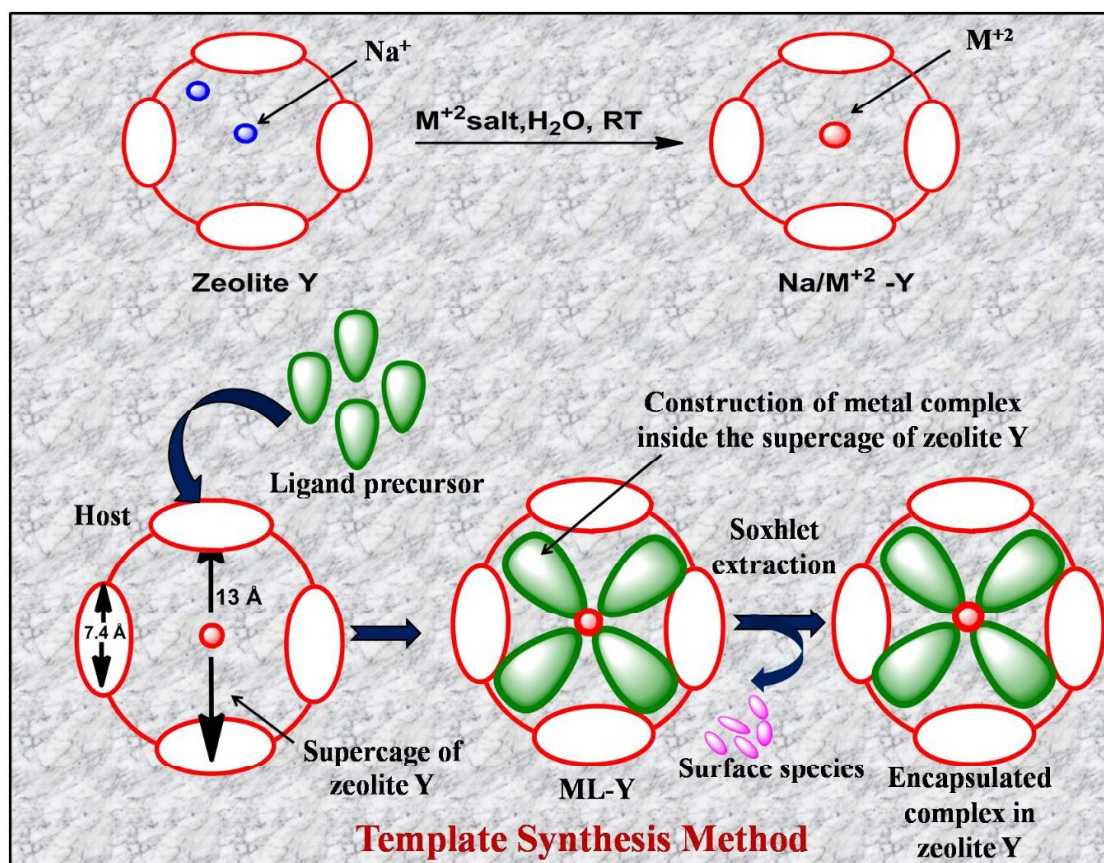


Figure 1.4: Synthesis of M/Na-Zeolite –Y and encapsulation of 'ship-in-a-bottle' metal complex in void of zeolite via 'template synthesis method'.

1.1.3.3 Zeolite synthesis method

Another method for the synthesis of metal complexes inside the zeolite, is the zeolite synthesis method. In this method, the metal complex which is to be encapsulated is added to the reaction mixture during the crystallization of the zeolite (shown in Figure 1.5). Thus crystallization of the zeolite occurs around the guest metal complex. It is template synthesis type approach where the complexes act as a template and this is finally trapped within the zeolite framework. The zeolite can be synthesized from the silica source dissolved in sodium hydroxide solution. The desired metal complex is added to the reaction mixture and stirred for 30 minutes. Aluminium isopropoxide dissolved in sodium hydroxide, is then added and the resulting gel is autoclaved at 363 K for 24 h. Purification of the product is completed with Soxhlet extraction.

Fundamental requirements for this process are the sufficient solubility of complex in the zeolite synthesis medium along with good thermal stability, pH and temperature resistivity to complete the

process. This is a method, where building of a host framework around the guest molecule takes place. The essential condition is that the presence of the complex must not modify the windows of the zeolite host framework. Balkus *et al.* has synthesized the encapsulated transition metal (cobalt and copper) complexes of perfluorophthalocyanine in zeolite X and Y by using zeolite synthesis method.⁴⁷ Balkus and group members have claimed that homogeneous encapsulation of the metal complexes in zeolite is possible by avoiding the aggregation of the complex molecules in the aqueous synthesis medium during the zeolite synthesis.⁴⁸ Encapsulation of phthalocyanine, porphyrins and amino acids complexes are synthesized by using this procedure. This method actually encapsulates only the distinct metal complexes with complete accuracy because pure metal complexes are used as template for zeolite synthesis and the process therefore is devoid of presence of any uncoordinated ligands or metal ions.

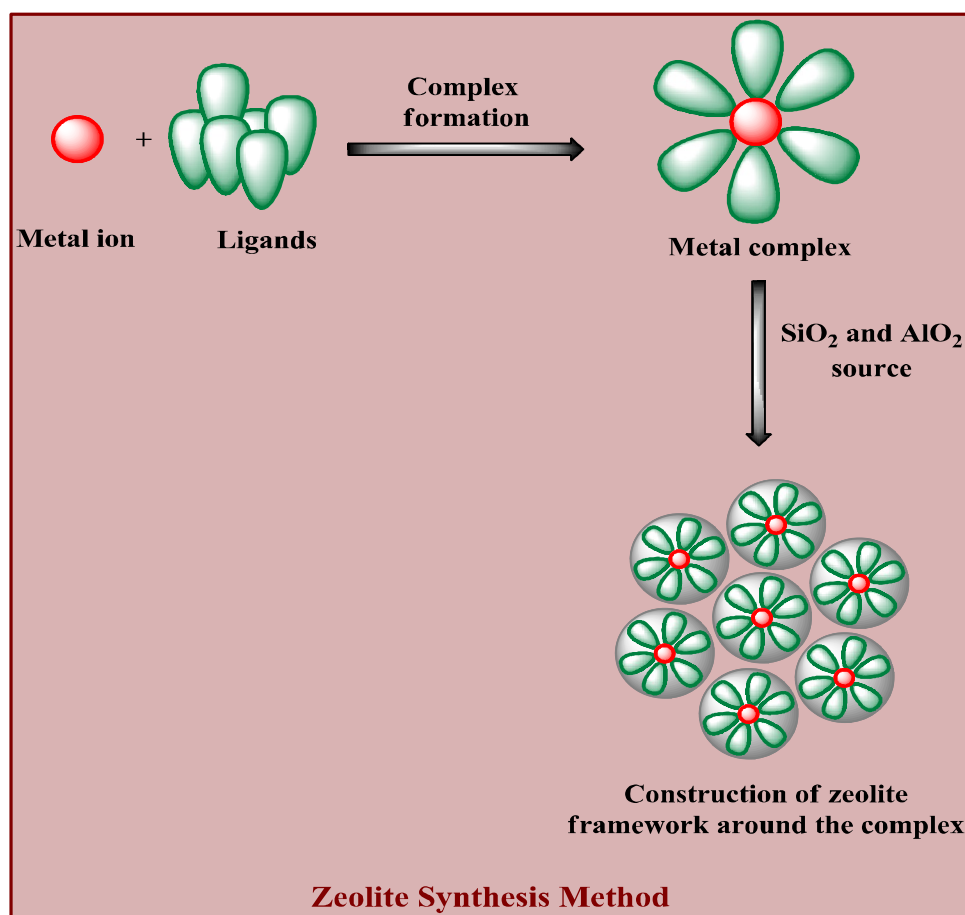


Figure 1.5: Encapsulation of 'ship-in-a-bottle' metal complex in void of zeolite via 'zeolite synthesis method'.

1.1.4 Zeolite encapsulated metal complexes as heterogeneous catalysts

Zeolite encapsulated metal complexes of phthalocyanine, porphyrins and Schiff-base ligands are already well-established efficient catalysts for several oxidation reactions like oxidation of phenols, alcohols, carbonyl compounds, alkenes and carboxylic acids and often play crucial role in industrially important catalytic reactions. In general, the homogeneous catalysts are also proficient for such type of reactions under mild reaction conditions, however, there are certain disadvantages associated in terms of stability, deactivation of catalyst due to aggregation or dimer formation, difficulty in separation from reaction mixture, lack of reusability etc. All these issues could be efficiently resolved by encapsulating these metal complexes within the voids of zeolites. Here host framework actually provides the special steric and electronic environment and also thermal stability to the guest metal complexes. Furthermore, encapsulated metal complex usually exhibits altered functionality and selectivity. All these advantages of the encapsulation leading to the modified functionality have become the primary driving factors for designing innovative and attractive catalysts. For example, encapsulated metal salen complexes have been successfully employed as catalysts for the epoxidation, oxidation of phenols, direct oxidation of methane to methanol and oxidation of *p*-xylene to terephthalic acid. These hybrid systems have proficient potential for the various oxidation reactions such as oxidation of aliphatic and aromatic hydrocarbons, alcohols etc.⁴⁹⁻⁵¹ One remarkable study is based on the excellent capacity of the zeolite encapsulated amine-functionalized ionic liquids which captures atmospheric CO₂.⁵² Encapsulated Fe(III) - Schiff base complexes illustrate a potential ability for the oxidative coupling of 2-naphthol as compared to their homogeneous analogues.¹³ Encapsulated Co-Salen complex is known as an effective catalyst for the oxidation of cyclohexane⁵³ whereas encapsulated copper complexes with 14-membered hexa-azamacrocycles exhibit superior catalytic activities for the oxidation of tetrahydrofuran with selectivity.⁵⁴ Zeolite encapsulated metal-salen complexes have been studied for the catalytic activities for many reactions such as decomposition of H₂O₂ and tert-butylhydrogenperoxide (TBHP).⁴⁹

One of very exciting reports has huge impact in this field is based on the encapsulation of iron phthalocyanine complexes within the supercages of zeolite-Y,⁵⁵ incorporated in a polydimethylsiloxane (PDMS) membrane (shown in Figure 1.6). Here polymer corresponds to a phospholipid membrane in which cytochrome P-450 exist. This hybrid catalytic system shows the realistic mimicry of cytochrome P-450 enzyme as well as efficient catalytic activity towards the oxidation of alkanes which essentially makes the catalyst industrially important. This hybrid system is capable for the oxidation of alkanes at room temperature at a very similar rate as that of the enzyme.

The observation of the preferential oxidation of tertiary C-H bonds recommend a close mechanistic similarity to the enzymatic process.

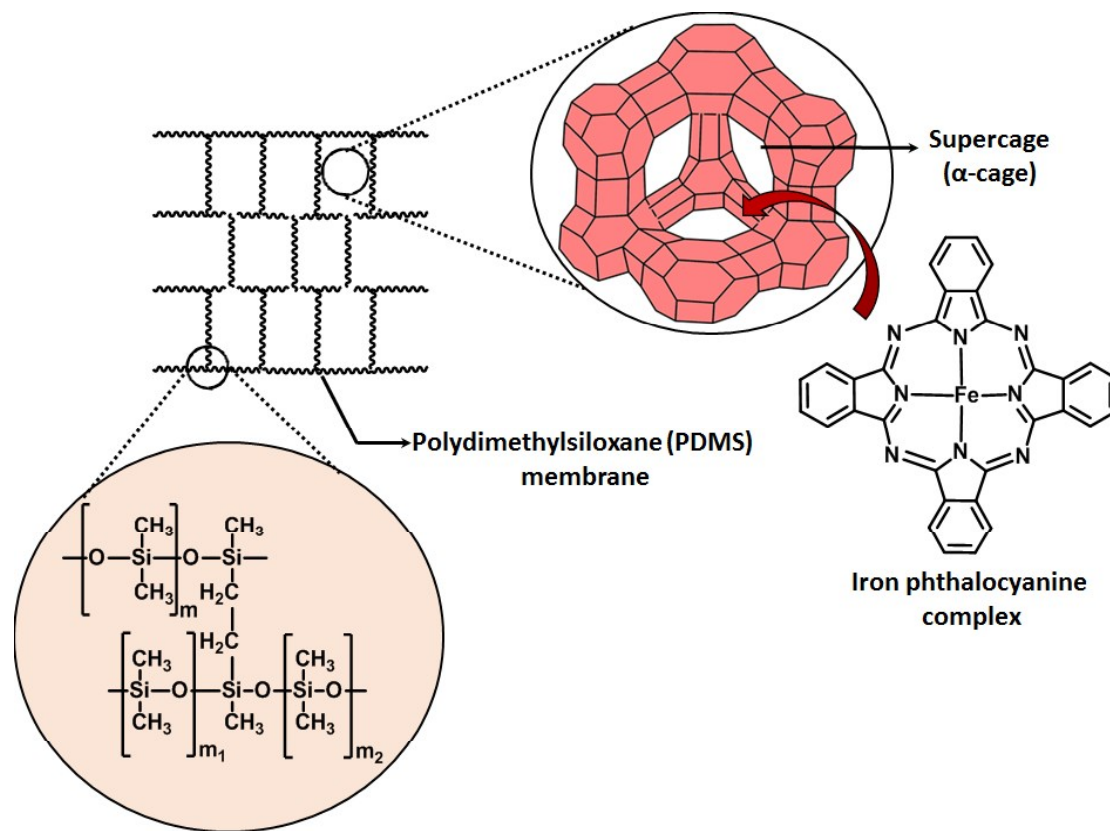


Figure 1.6: Structural architecture of the zeolite-Y encapsulated iron phthalocyanine complex (FePcY-PDMS) incorporated in a polydimethylsiloxane membrane.⁵⁵

Herron's group reported Fe(II) phthalocyanine complex encapsulated inside the supercages of zeolites NaX and NaY and these systems are employed as catalyst for the oxidation of alkanes in presence of iodosobenzene. Upon encapsulation, improved yield and selectivity are the outcome.⁵⁶ Actually there are several reports available in literature which mainly discuss the altered and finally improved catalytic activities of zeolite encapsulated metal complexes. Some of these complexes are summarized here. Encapsulated Fe-phthalocyanine catalyst is efficiently utilized for the aerobic oxidation of hydroquinone, oxidation of 1-octene and oxidation of cyclohexene. The catalyst is found to be stable towards self-oxidation is found four times more efficient than its free-state.⁵⁷

Oxidation of cis-pinane is carried out by the zeolite-NaY encapsulated iron or cobalt phthalocyanines complexes (MPcNaY) in presence of TBHP as oxidant at room temperature⁵⁸ to the major product 2-pinane hydroperoxide. Other products of the oxidation of pinane such as pinocampheol, verbanol and the corresponding ketones are not obtained in the reactions when MPcNaY are the catalysts however these products are observed in presence of free-state complexes. This effect has been explained in terms of specific orientation of the substrates approaching to the metal active sites indeed governed by the well-defined zeolite host architecture.

The oxidation reaction of cyclohexane is studied in presence of encapsulated phthalocyanines and substituted (Cl- and NO₂-) phthalocyanines complexes of copper, cobalt and iron in zeolites X and Y as catalysts. Molecular oxygen and alkyl (tertiary butyl, cyclohexyl and cumyl) hydroperoxides are used as oxidants. The catalytic activity of the encapsulated systems is much higher as compared to the free-state analogs because encapsulation causes site isolation of active centers. Rate of oxidation reaction decreases with an increase of the molecular cross-section of alkyl hydroperoxides and the reactivity order is appeared as cyclohexyl>t-butyl>cumyl hydroperoxides. Therefore, author's claim about the location of the active site within the cavities of zeolite becomes a valid argument.⁵⁹ Iron phthalocyanine (FePc) and cobalt phthalocyanine (CoPc) complexes in free-state as well as encapsulated state in zeolite-Y are employed as catalysts for the aerobic oxidation of hydroquinone. A significant enhancement of reaction rate substantiates the encapsulated CoPc-Y complex, an active catalyst, however its free-state analogue is completely inactive. The site isolation is mainly responsible for the enhanced activity.⁶⁰

A detailed characterization of the zeolite encapsulated M(II) phthalocyanine complexes (M = V, Co and Cu) is carried out with the help of chemical and thermal analyses, FT-IR, diffuse reflectance UV-Vis and EPR spectroscopic techniques. The encapsulated phthalocyanine moiety undergoes structural alteration from its original square planar geometry and hence shows enhanced catalytic activity for phenol hydroxylation reaction as compared to its free-state. A comparative study has revealed that the activity of the encapsulated M(II) phthalocyanine complexes can be associated with the redox potential of the M⁽ⁿ⁺¹⁾/Mⁿ⁺ couple of the central metal atom.⁶¹

Oxidation of cyclohexene is also catalyzed by the zeolite Y encapsulated metalloporphyrins in presence of tert-butyl hydroperoxide. The authors have discussed about the electrostatic interaction between the host framework and guest cationic metalloporphyrins. This hybrid system shows high catalytic activity.⁶²

Zeolite encapsulated $\text{Ru}(\text{bpy})_3^{3+}$ complex is employed as catalyst for the oxidation of water. Here, catalyst oxidizes the water slowly but with high efficiency. Study has claimed that encapsulated system eliminates the multi-molecular degradation pathways which is usually observed in solution and the rate of reaction is dependent on the acidity of zeolite framework. Encapsulation of molecules inside the zeolite cages allows to follow the chemical path of the reaction which is not feasible under usual homogeneous conditions as homogeneous catalysis follows multi-molecular reaction pathways.⁶³ Dutta and coworker have reported the synthesis of zeolite encapsulated oxobis(2,2'-bipyridine)ruthenium(IV) complex by air oxidation of bis(2,2'-bipyridine)aquaruthenium(II) complex where encapsulation stabilizes the $[\text{RuII}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$ complex in its higher oxidation states. In solution state, such complexes have tendency to dimerize upon oxidation and form the μ -oxoruthenium(III) complex. In the zeolite cages, steric constraints imposed by the walls of zeolite help to stabilize the mononuclear complex and well supported by molecular modeling. Dehydration of the zeolite framework offers an environment where electrostatic fields support the deprotonation and air oxidation of Ru(III) to Ru(IV).⁶⁴

Another report discusses the synthesis of zeolite encapsulated Fe(III) and Ni(II) complexes of 2,2'-bipyridine and 1,10-phenanthroline mixed ligand are synthesized by using *in situ* method. and these systems are found to be active catalysts for the decomposition of H_2O_2 and for the oxidation of o-phenyl phenol (OPP)⁶⁵

Zeolite encapsulated transition metal complexes of amino acids are emerged as really promising catalysts for the epoxidation of olefins and oxidation of cyclohexane and alcohols.^{66, 67} Transition metal complexes of salen ligand are synthesized in neat state as well as inside the zeolite and employed as catalysts for many reactions. These complexes show good catalytic activity after encapsulation.^{49, 68-70}

Fe(III) Schiff-base complexes have been encapsulated inside the supercages of different alkali exchanged zeolites (LiY, NaY, and KY) by flexible ligand method (FLM).¹³ The zeolite encapsulated Fe(II) Schiff-base complexes are employed as catalysts for the oxidative coupling of 2-naphthol (shown in Figure 1.7). Iron complexes encapsulated in potassium exchanged zeolite-Y are found to be most efficient for catalytic conversion of 2-naphthol to binaphthol (BINOL) and produces higher selectivity towards the R-conformation. Authors have claimed that catalyst with a more negative reduction potential acts as better catalyst for the conversion of 2-naphthol.

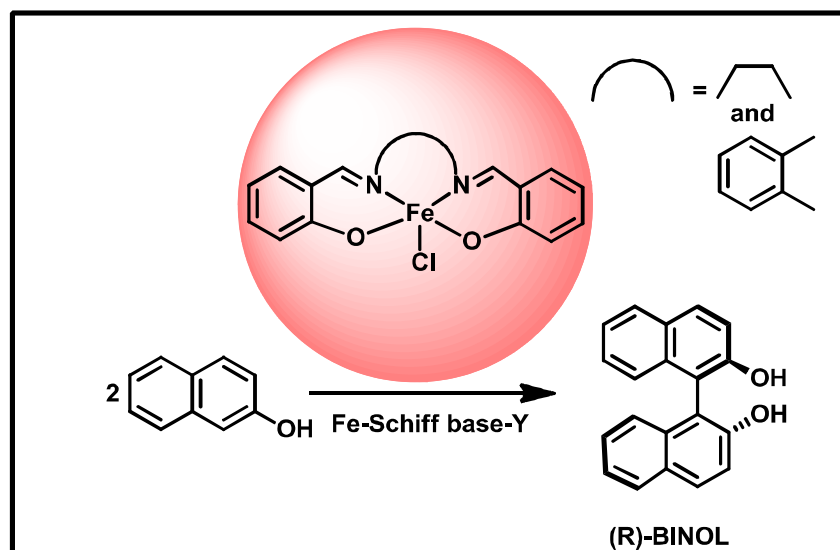


Figure 1.7: Schematic representation for the conversion of 2-naphthol to binaphthol (BINOL) catalyzed by Fe(III) Schiff-base complexes encapsulated in zeolite-Y.¹³

Recently, our group also has reported the detailed characterization and catalytic activity of some M(II) salen complexes, which are encapsulated inside the zeolite-Y and MCM-41.⁷¹⁻⁷⁵

Very recently, Selvaraj and co-workers have published a report based on the zeolite-Y encapsulated Cu(II) phthalocyanine and tetra-chloro substituted Cu(II) phthalocyanine complexes.⁷⁶ DFT studies of these complexes identifies that the walls of the zeolite framework impose steric constraint and modify the properties of the guest metal complex. Hence alter the values of the global, local, and Fukui function values of the guest complexes which in turn, modifies the catalytic activities (shown in Figure 1.8).

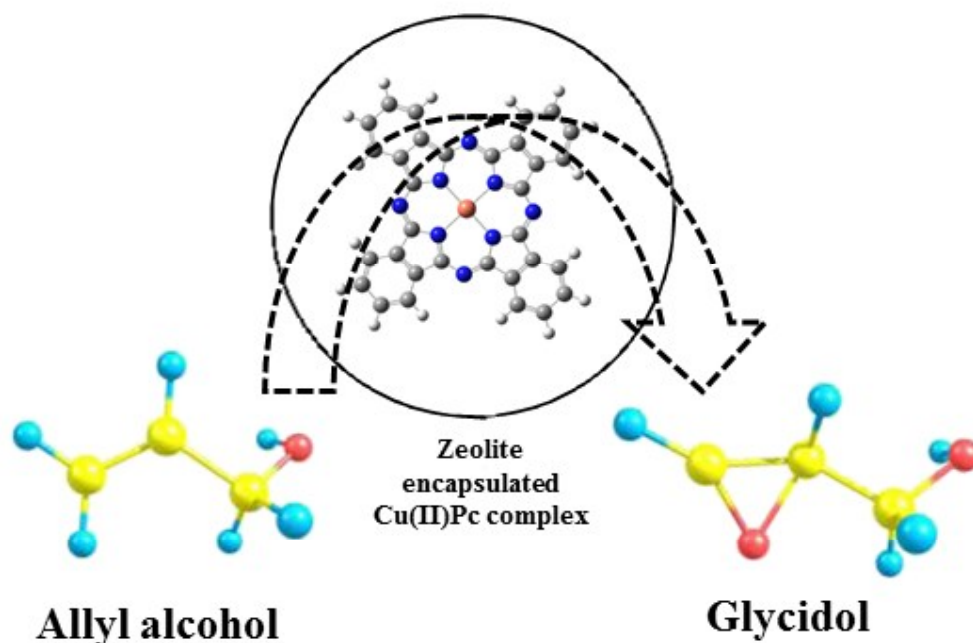


Figure 1.8: Schematic representation for the conversion of allyl alcohol into glycidol catalyzed by Cu(II) phthalocyanine complex encapsulated in zeolite.⁷⁶

1.1.5 Zeolite encapsulated metal complexes: Structural Aspects

The zeolite encapsulated systems are extensively studied however the structural modifications adopted by the encapsulated guest complexes trapped within the supercages of zeolite is comparatively less explored area. The typical architecture and topology of the zeolite framework could have profound effect on the structure as well as electronic and magnetic properties of the guest complex.

One of the earliest report by Mizuno and Lunsford is on tris(2,2'-bipyridine)cobalt(II) complexes in the supercage of zeolite Y. Different spectroscopic techniques and electron paramagnetic resonance studies indicated that zeolite encapsulated $[\text{Co}(\text{bpy})_3]^{2+}$ complex undergoes an exciting temperature driven inter-conversion from high spin ground state to low spin, whereas its free-state analog remains in high spin ground state both in its solution and solid states (shown in Figure 1.9).⁷ It was reported that the spin behavior is intra-molecular in nature probably due to the fact that the zeolite supercage enforces the $[\text{Co}(\text{bpy})_3]^{2+}$ complex ion to adopt an octahedral geometry less distorted than in the encapsulated state.⁷⁷ The space constraints imposed by the zeolite walls, the net negative charge of the zeolite framework and the distribution of the positive charges of the alkali cations can lead to specific

interactions between the complex and the zeolite framework which in turn makes structural and functional variations.

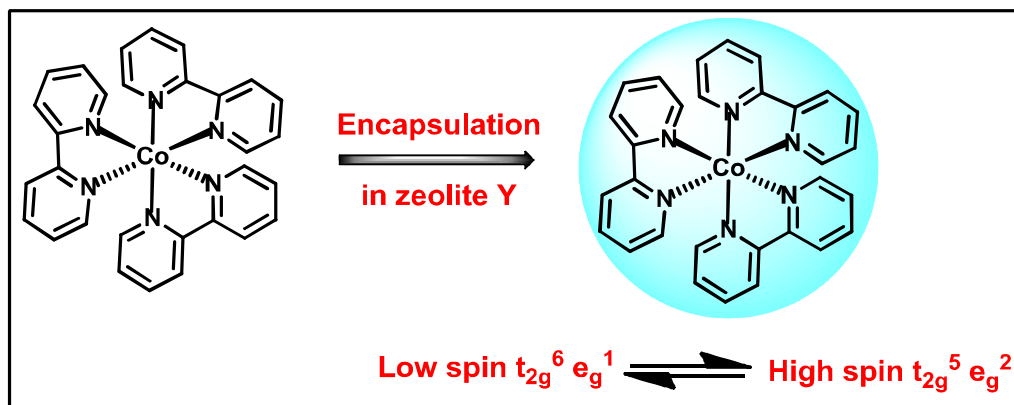


Figure 1.9: Schematic representation for the Tris(2,2'-bipyridine)cobalt(II) Complexes in Zeolite Y.⁷

A report on encapsulation of iron(III) complexes with N,N-bis(salicylidene) ethylenediamine (salen) and N,N-disalicylidene-1,2-phenylenediamine (salophen) ligands in zeolite Y has concluded that the complexes adopt a pseudo-square-pyramidal geometry upon encapsulation thereby causing an alteration in HOMO and LUMO energy levels. The diffuse reflectance UV-Vis spectra of the encapsulated systems show a dramatic red shift of the charge transfer band with increasing electropositive character of the exchangeable cations. The reduction potentials are shifted towards negative values with increasing size of the exchanged alkali metal cations. Metal complexes encapsulated in potassium exchanged zeolite-Y are found to be more effective for catalytic conversion of 2-naphthol to BINOL.¹³

A comparative spectroscopic and magnetic investigation of the cobalt phthalocyanine (CoPc) complex encapsulated in zeolite Y and in the un-encapsulated state has reported that when square planar CoPc (end to end diagonal = 15 Å) is trapped in zeolite Y supercage (diameter 12.7 Å), it undergoes 'saddle' type of distortion thereby lowering the symmetry (shown in Figure 1.10A). Encapsulation has caused a dramatic change in the magnetic property of the complex; there is an enhancement of magnetic moment of complex. Distortion in the geometry of the guest complex imposed by topology of the host cavity causes the lowering in energy difference between the low-spin doublet ground state and the higher lying high spin quartet state making the later thermally accessible.⁷⁸ In the recent times, the effect of different host topology has been investigated. Nickel salen complex shows pragmatic changes

in its magnetic behavior when the complex is encapsulated in zeolite Y but remains similar to solution-state behavior in MCM-41 (shown in Figure 1.10B).⁷¹

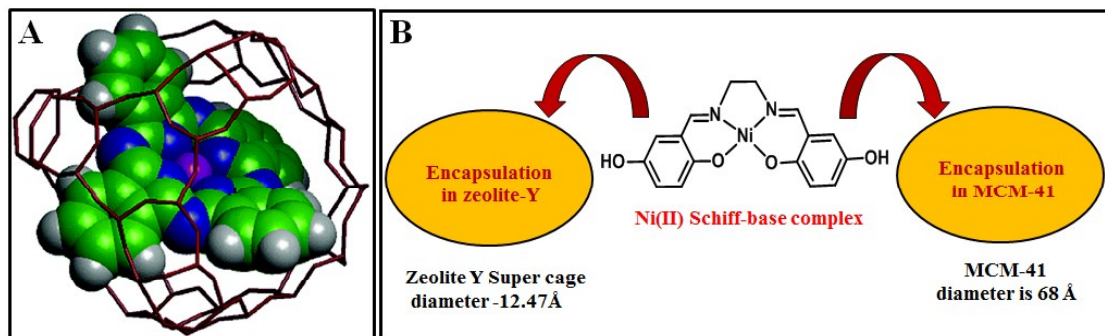


Figure 1.10: Schematic representation for (A) cobalt phthalocyanine (CoPc) complex and (B) nickel Schiff-base complex encapsulated in zeolite-Y and MCM-41.^{71, 78}

Another spectrochemical study shows that encapsulation or tethering of the metal complexes leads to the red shift of the MLCT as well as intra-ligand transitions. DFT studies provide additional support to the structural changes of the guest system as it shows lifting of HOMO and LUMO levels under the influence of the space constraint as well as the coulombic electrostatic field imposed by the zeolite mantle.⁷⁹ UV-Vis and EPR results, have altogether proposed the distorted saddle type geometry of CuPc encapsulated within the supercage of zeolite-Y, in which alternate isoindole rings of the Pc molecule are staying the out of plane of the molecule. This type of distortion leaves the central C_8N_8 ring essentially planar.⁸⁰

Copper(II) salicylidene-p-aminobenzoic Schiff base complex when encapsulated in zeolite Y, the guest complex is found to adopt the distorted tetrahedral geometry. However, in case of Cu exchanged zeolite-Y Cu(II)-Y, the geometry around the copper metal adopts tetragonal geometry. The report has revealed the fact that the encapsulated complex and Cu(II)-Y, both systems are capable for CO adsorption, however the capacity of CO adsorption is linked up with the geometry around the metal center of the complex. The encapsulated complex in zeolite Y have been found more efficient for CO adsorption due to the higher charge density on the metal center as compared to that Cu(II)-Y.⁸¹

Viswanathan and co-workers have studied Bis(ethylenediamine)Cu(II) complex encapsulated in the faujasite type zeolite (shown in Figure 1.11), with the help of different spectroscopic techniques and electron paramagnetic resonance (EPR) spectrum. The findings have clearly indicated a distinctly different geometry that the complex adopts upon encapsulation. DFT studies have revealed an

appreciable changes observed in HOMO and LUMO energy levels after encapsulation. Besides that, the encapsulated complex has shown better catalytic activity towards the oxidation of dimethyl sulfide. Authors have concluded that zeolite matrix is responsible for these structural and functional changes.⁸²

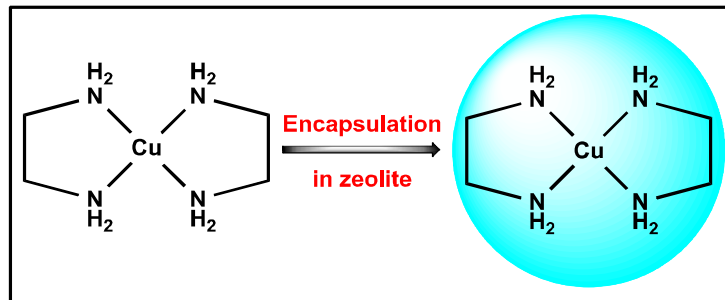


Figure 1.11: Schematic representation for the Bis(ethylenediamine)Cu(II) complex encapsulated in the faujasite zeolite.⁸²

Very recently, the influence of the different zeolite framework such as LTL, MWW and zeolite Y on the geometry of Pt(II)tetraammine complex has been studied (shown in Figure 1.12). The theoretical observations indicated the space constraint imposed by the walls of zeolite framework on the encapsulated metal complex, actually alters the structural and catalytic behavior of the guest complex. The encapsulation modifies the magnitude of redox potential, which in turn causes modified catalytic behavior. DFT calculation shows the decrease in HOMO-LUMO gap that is basically originated by the space constraints and Coulombic electrostatic field engendered by the host topology. Square planar geometry of the Pt(II)tetraammine complex acquires a nonplanar geometry when encapsulated inside the supercage of zeolite. Extent of distortion is most pronounced in LTL zeolite framework than that in MWW and zeolite Y, however, integrity of zeolite framework is restored.⁸³

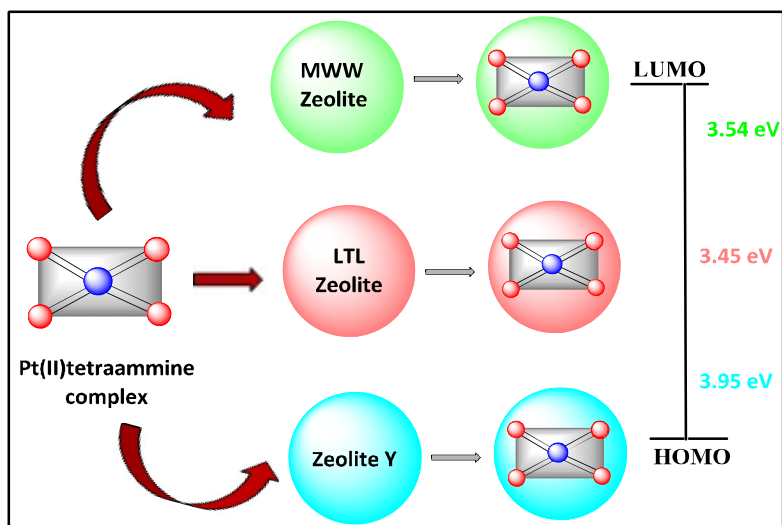


Figure 1.12: Schematic representation for the Pt(II)tetraammine complex encapsulated in the different zeolite framework (LTL, MWW and zeolite Y).⁸³

To investigate the adopted geometry of encapsulated complex, the different characterization techniques may be very informative. To explore the changes in the ligand geometry of the guest metal complex, UV-Vis, IR and other spectroscopic studies can be used, whereas the magnetic measurements, electronic spectroscopic studies, XPS will facilitate to determine the geometry around the metal.

A recent publication is based on the synthesis of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane nickel(II) complex inside the cavities of zeolite-Y as well as its neat state and their activity for the photocatalytic removal of methylene blue under visible light (shown in Figure 1.13).⁸⁴ The flexible ligand method is used for the encapsulation of the Ni(II) complex inside the zeolite Y. The DFT studies exhibit the changes in the structural parameters and HOMO–LUMO energies provide useful information about the nature of the host–guest interaction and hence the reactivity. The modifications in energy levels and structural parameters of the encapsulated metal complex are originated by the constrained environment imposed by the zeolite framework. In addition, the zeolite encapsulated complex exhibits photocatalytic activity towards the degradation of methylene blue under visible light irradiation with reusability.

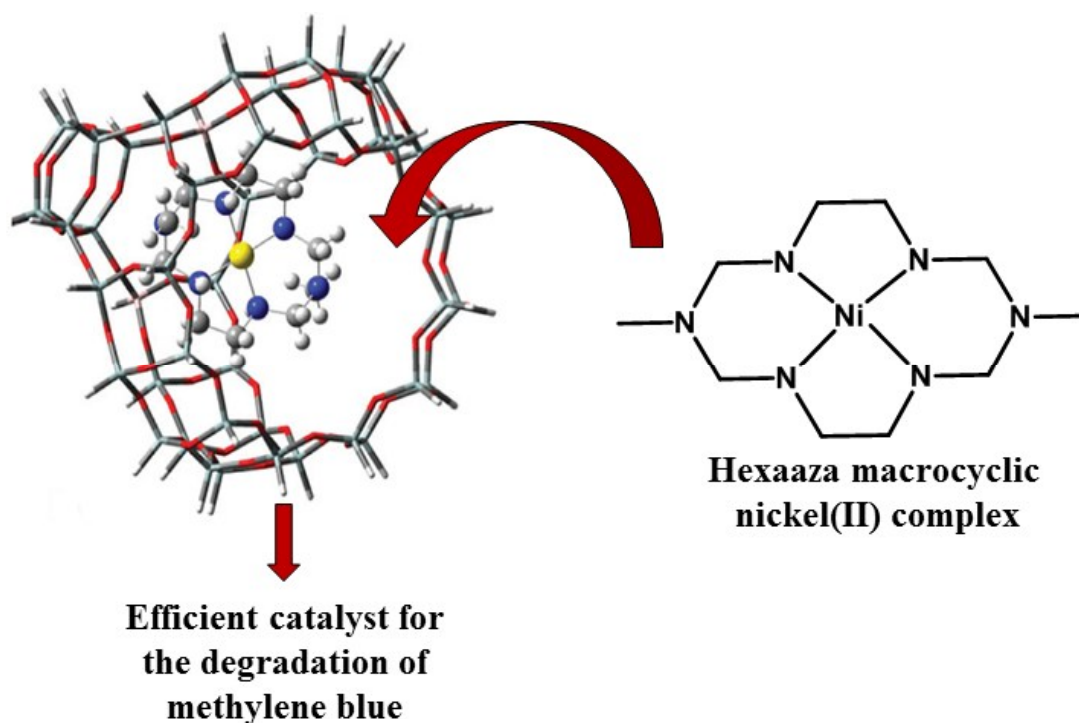


Figure 1.13: Schematic representation for the degradation of methylene blue catalyzed by zeolite encapsulated hexaazacyclotetradecane nickel(II) complex.⁸⁴

1.2 SCOPE OF THE PRESENT STUDY

The aim of the present thesis is to investigate the effect of size and topology of the framework of zeolite-Y on the structure and properties of encapsulated square-planar guest complexes since the structural modification triggers significant changes in their electronic and catalytic properties. Another target is to comprehend the correlation between structural modification and modified reactivity of the encapsulated guest complex. The square-planar metal complexes synthesized from different transition metals such as nickel, palladium, copper and cobalt with the Salophen and substituted salophen Schiff-base type ligands are under surveillance. For the comprehensive study, the ligands are so chosen, that they follow order of increasing molecular dimension or end to end distance in a series and could deliver different electronic environment to the central metal (guest metal complexes are presented in Figure 1.14). These zeolite encapsulated complexes along with their free-state analogs are well characterized with the help of different spectroscopic techniques (X-ray diffraction, electronic, vibrational and X-ray photoelectron, and electron dispersive spectroscopy/atomic absorption spectroscopy), scanning electron microscopy thermal analysis (thermogravimetric analysis,

differential scanning calorimetry and derivative thermogravimetry), magnetic measurements and DFT study.

Results obtained from all the above-mentioned techniques are thoroughly analyzed to know structural modifications of the encapsulated guest complex. IR spectroscopic studies furnish information about the ligand moiety of the complex. On the other hand, electronic spectroscopic studies, XPS, magnetic studies render information about the geometry around the central metal ion. The present thesis have been restricted to the Ni(II) (d^8), Pd(II) (d^8), Co(II) (d^7) and Cu(II) (d^9) transition metal complexes. Magnetism of both d^7 and d^8 systems in square-planar ligand field are sensitive and diagnostic of the nature of structural deviation around the metal ion. These zeolite encapsulated metal salen complexes are synthesized by *flexible ligand method*. Structural integrity of the host moiety is supported by Powder XRD studies. Electronic, vibrational and X-ray photoelectron spectroscopy provide the evidence for the formation of the complex within the supercages of zeolite-Y. Spectroscopic and magnetic studies indicate a significant deviation of the structure adopted by the guest complex as compared to its neat form. These synthesized encapsulated metal complexes are employed as catalysts for several catalytic reactions like oxidation of styrene, Heck-coupling reaction and degradation of rhodamine B. The electronic effect of the different substituent groups attached on the ligand moiety in the catalyst play an important and decisive role for the reactivity of these catalysts in the homogeneous phase. On the other hand, after the encapsulation within the voids of zeolite Y, functionality of these hybrid systems is mainly governed by the extent of steric constraint imposed by the host topology on the guest complexes. Upon encapsulation, all these factors play a crucial role in tuning the electronic properties of the catalyst and hence the functionality of that system for a particular catalytic reaction. Electronic behavior is also well-supported by DFT studies.

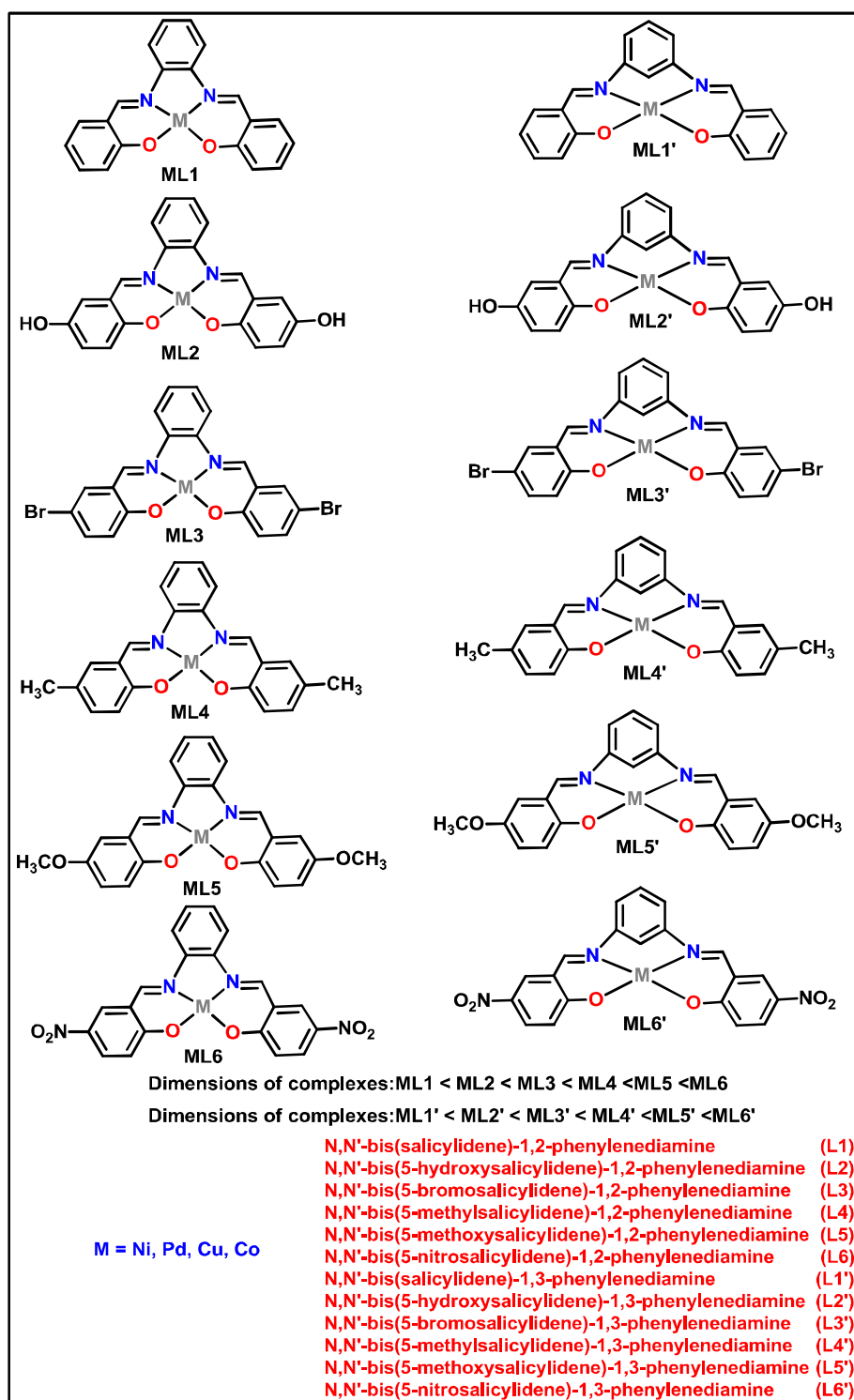


Figure 1.14: Schematic representation of the M(II) Schiff-base complexes with different-different molecular dimensions (end-to-end distance).

Comparative structural and catalytic studies of these metal Schiff-base complexes are under consideration for the current thesis with the additional motif to observe the effect of site isolation. Comparative studies reveal a quite fascinating correlation existing between the catalysis and modified electronic structure of the encapsulated complexes which subsequently leaves a lot of opportunities to further modify the activity of the catalysts and to have a better insight towards these heterogeneous host-guest catalytic systems.

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