



Chapter 7:

Conclusions and Future Scope

7.1. Scope and Nature of present study

Distinctive micro porous architecture of zeolite Y provides a literally fascinating way of heterogenization of homogeneous catalysts. Transition metal Schiff-base complexes encapsulated in zeolite Y are of a distinctive class of heterogeneous catalysts with suitable molecular dimensions and flexible ligands, that's why these hybrid systems are an attractive research area in recent times. These 'hybrid catalyst' are well known mimics of several biological enzymes such as cytochrome-P450, hemoglobin etc. whereas the 3D structure zeolite Y plays the role of protein mental and provides the analogous steric confinement to the guest complex and substrate holding sites for the catalytic process. The encapsulated guest complex has shown functional analogy with the metal porphyrin complex which is present in 3D protein sheath and responsible for the catalytic activity of biological processes. These 'hybrid class' of catalysts are also known as “zeozymes” and have proven the remarkable catalytic activities for the various organic transformations especially catalytic oxidation of C-H bonds, dye degradation etc. Many frequent reports are available which deal with the customized catalytic activity of these hybrid heterogeneous systems however comparatively fewer reports are available exploring the detailed characterization of the structure adopted by the guest complex under encapsulation. Most importantly, even lesser number of reports in literature really establishes the link between modified geometry and altered reactivity of such systems under encapsulation. In the present work we have explored the consequence of the zeolite framework on the structural and functional aspects of the encapsulated system by using different characterization techniques and theoretical studies to understand the effect of the extent of distortion in the geometry of guest complex and its relation with the adopted reactivity of the hybrid encapsulated system.

In the present study, the square-planar complexes of different transition metals (Ni, Pd, Cu and Co) Schiff-base metal-salen and substituted metal salen complexes have been synthesized, maintaining the increasing molecular dimension (average end-end distance) in a series for detail study. Encapsulated complexes are well characterized with the help of different spectroscopic techniques (X-ray diffraction, electronic, vibrational and X-ray photoelectron, and electron dispersion spectroscopy/atomic absorption spectroscopy), scanning electron microscopy, and

magnetic measurements and also studied by Density Functional Theory. Results of all the above-mentioned measurements altogether have been explored to acquire the plausible structure of the encapsulated complex. Information obtained from the IR spectroscopic studies for these complexes pertains mostly to the ligands, whereas magnetic studies and electronic spectroscopic studies, on the other hand, provide information about the geometry around the metal-ion. The present studies are restricted to the Ni(II) (d^8), Pd(II) (d^8), Co(II) (d^7) and Cu(II) (d^9) metal complexes, since magnetism of d^7 , d^8 and d^9 systems in square-planar ligand-fields is both sensitive and diagnostic of the nature of deviation from the planar geometry.

The thesis is divided into seven chapters and chapter 3 has three parts (3A, 3B and 3C). Conclusion of the various chapters is briefly discussed as follows:

Chapter 1

This chapter presents the general discussion about zeolites, their structures constituents. Along with this a brief introduction about the zeolite encapsulated metal complexes essentially known as biomimetic heterogeneous catalysts and different synthetic approaches like “flexible ligand synthesis”, “template synthesis method” and “zeolite synthesis method” to synthesize the such systems are briefly reviewed. Furthermore, advantages of heterogeneous catalyst over the respective homogeneous counter parts also are discussed and literature surveys on the catalytic activity of these systems on the various organic transformations are presented in concise tabular form. Beside this, some prominent reports on the characterization with experimental and theoretical support of the adopted geometry of guest complex under encapsulation and its consequences on the spectroscopic, redox and magnetic behavior are also discussed.

Chapter 2

This chapter deals with the materials, methodologies used for the synthesis of transition metal (Ni, Co, Cu and Pd) complexes of Schiff-base ligands with general formula: N,N' -bis(salicylidene)ethylenediamine (L1), N,N' -bis(4-hydroxy-salicylidene)ethylenediamine (L2), N,N' -bis(5-hydroxy-salicylidene)ethylenediamine (L3), N,N' -bis(5-bromo-salicylidene)ethylenediamine (L4), N,N' -bis(5-methyl-salicylidene)ethylenediamine (L5) and N,N' -bis(5-methoxy-salicylidene)ethylenediamine (L6) Schiff-base metal complexes in free and

encapsulated states and synthesis of MCM-41. Catalytic reactions of oxidation of styrene, sulfoxidation of methyl phenyl sulfide and degradation of rhodamine B have also been discussed in this chapter along with the brief introduction about the different characterization tools like elemental analysis, AAS, XPS, XRD, SEM, FTIR spectroscopy, Solid and solution phase UV-visible spectroscopy and magnetic susceptibility measurement (SQUID) and gas chromatography (GC) required to study catalytic reactions. The theoretical model of the DFT (Density Functional Theory) for the zeolite encapsulated nickel complexes also are mentioned in this chapter.

Chapter 3

Nickel Schiff-base complexes in free as well as encapsulated state are discussed in chapter 3 which comprises three parts (3A, 3B and 3C) to explore the different aspects of the study of encapsulated systems.

Chapter 3A deals with the steric confinement of the NiL₃ complex under encapsulation in two different hosts (MCM-41 and zeolite Y) via flexible ligand synthesis method and the consequences are discussed with the help of different experimental studies with theoretical support which definitely indicate that the distorted geometry of the NiL₃ complex is mainly accountable for the blue shift of the d-d band in electronic spectra, enhancement of the magnetization. However the larger voids of mesoporous MCM-41 encapsulates the complex without any significant loss of planarity, which also acts as a backbone of the prior argument

In Chapter 3B, the another dimension of the study has been explored, where three nickel Schiff complexes (NiL₁, NiL₄ and NiL₆) having different molecular dimensions are encapsulated in zeolite Y via flexible ligand synthesis method. The modified functionalities offered by the different complexes evidently signify that after encapsulation, the topology of the host supercage has profound impact on the geometry the encapsulated complexes adopt. Ni(II) salen complexes in free state act quite differently and show diamagnetism while after encapsulation in zeolite Y, all of them show enhanced magnetisation and significant blue shifts of the d-d transition. Higher the molecular dimension, greater is the extent of distortion of the geometry and as a consequence the greater is reactivity of the complex in the entrapped state

Therefore the encapsulation actually governs the electronic factors of the encapsulated complex via the steric confinement.

Chapter 3C is the extension work of chapter 3B which deals with the encapsulation of nickel Schiff-base complexes in zeolite Y via flexible ligand synthesis method. It is quite evident that -OH group in the 4th position does not participate electronically towards the catalytic reaction as anticipated. Therefore the major contribution of the -OH substitution at that particular position (meta positions with the respect of (O-Ni) co-ordination site) is to primarily increase the bulk and molecular dimension of the complex, more the molecular dimension, more is the extent of distortion expected in the geometry of the complex under encapsulation. Therefore encapsulation leads distortion in geometry of the complex which play decisive role towards catalytic activity.

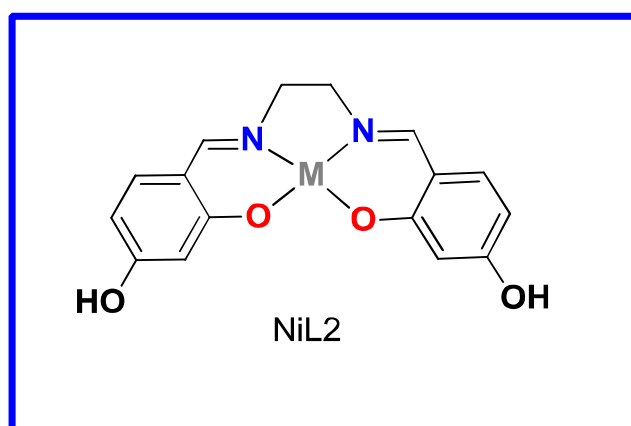


Figure 7.1: Structure of NiL2 complex.

Chapter 4

Chapter 4 discusses the synthesis of palladium Schiff-base complexes in free and encapsulated state in zeolite Y. The molecular dimension of complexes follows the order as: PdL1<PdL3<PdL4<PdL5<PdL6. These systems are well characterized and employed as catalysts for the sulfoxidation of methyl phenyl sulfide. The balances between steric and electronic effects of different substituents attached on the complexes are quite prominently observed via catalytic reactivity studies. On comparison with the neat states, encapsulated complexes are more efficient catalysts for the conversion of methyl phenyl sulfide to

corresponding sulfoxide and fascinatingly reactivity of encapsulated systems are mainly controlled by the extent of space constraint imposed by the host framework of zeolite Y.

Chapter 5

In this chapter, copper Schiff-base complexes (CuL1, CuL3, CuL4 and CuL6) on the basis of their increasing order of the molecular dimensions are encapsulated inside nearly spherical supercage of zeolite Y and are well characterized. They are employed as catalysts for the styrene oxidation reaction. It is observed that the alteration in the geometry of the complex plays a crucial role again for the modified reactivity of the system. Blue shifted d-d bands in electronic spectra indicate the alteration of the metal d orbital's energy levels. Furthermore, the observed shift towards higher binding energy in Cu_{2p_{3/2}} (II) XPS signal for the encapsulated complexes is observed which apparently indicates the generation more susceptible electropositive metal center for the nucleophilic attack. Larger molecular dimension causes more twist in geometry of complex and as an outcome, more susceptible metal center is produced for the nucleophilic attack.

Chapter 6

In this chapter, the study of square planar cobalt Schiff-base complexes in zeolite Y is presented. It is observed that the guest complex undergo distortion in geometry after encapsulation in zeolite Y which is reflected in electronic spectra or magnetic behavior of the encapsulated complex. Apart from this, the encapsulated complex has shown better catalytic activity for degradation of rhodamine B since reactivity of the encapsulated complexes are mainly governed by extent of distortion upon encapsulation.

7.2. Overall Conclusion of Present Work

- Synthesis of metal (Ni, Pd, Cu and Co) Schiff-base complexes in free as well as encapsulated state in zeolite Y is accomplished via flexible ligand synthesis.
- Detailed characterization of the complexes in both the state have been carried out with the help of different characterization tools like XRD, XPS, SEM-EDX, AAS, IR and UV-Vis spectroscopy, magnetic study.

- Detailed theoretical study has been pursued for the support the experimental observations and also to acquire clearer depiction of adopted geometry of encapsulated complex.
- Comparative catalytic studies have been presented for the both state complexes for various processes like oxidation of styrene, oxidation of phenyl methyl sulfide and degradation of rhodamine B. For all the cases, zeolite encapsulated complexes are found to be more efficient catalysts in comparison to their homogeneous analogues.
- Molecular dimensions of the complex in encapsulated state plays the decisive role for the catalytic activity. Complex with higher molecular dimension experiences higher degree of distortion and becomes more reactive for catalytic oxidation process. On contrary, in free state the reactivity of complexes are mainly controlled by the electronic factor of the substituent's which are attached on the phenyl rings.
- Distortion makes the metal center more reactive via making it stabilize in transition state where the nucleophile acquires axial position.
- Distortion can be introduced by the attaching electron withdrawing groups on complex or via the encapsulation of complex in zeolite Y. Interestingly, the electron withdrawing group (-Br) attached to the complex makes it more reactive even in its free state, while electron donating group (-OCH₃) present in the complex is least reactive but highly reactive after encapsulation since the complex have largest molecular dimension and experiences the highest degree of distortion in adopted geometry among the lot (Figure 7.2) which in turn, makes the metal center electron deficient and as a consequence more reactive

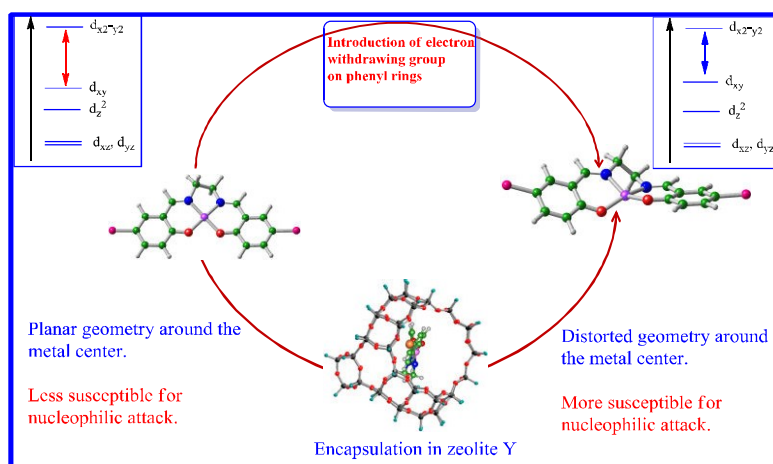


Figure 7.2: Encapsulation leads the distortion and makes the metal center more reactive for oxidation processes.

7.3. Future Scope

The link between modified geometry and catalytic activity of the zeolite Y encapsulated complexes actually leaves a huge scope of designing such heterogeneous systems to obtain better tunable reactivity with advantages of the heterogeneous systems so that they can play a vital role in the field of catalysis field. Therefore, present work can be comprehended in the following area of

- Designing of the different bio-inspired heterogeneous catalyst by via encapsulation of different metal complexes inside the zeolite-Y.
- Detailed characterization studies of the adopted geometry by different other tools to acquire the complete information of the metal environment.
- Detailed theoretical studies of such encapsulated complexes to understand other aspect of structural and functional modifications of these encapsulated systems.
- Various catalytic studies of such encapsulated systems for other organic transformations with a comprehensive understanding of the reaction mechanism of catalysis



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>