

ABSTRACT

In the last few decades, the encapsulation of metal complexes inside the voids of microporous zeolitic materials has received a great deal of attention of researchers as it provides a simple approach of coupling the reactivity of the metal complex with the robustness and stereochemistry of the host framework. Zeolite encapsulated metal complexes are well explored as heterogeneous catalysts in terms of enhanced reactivity or selectivity as compared to the homogeneous analogs. However, structural aspects of these encapsulated guest complex and the modified catalytic activities are yet to be harmonized in many cases. In the present thesis, the outcomes accomplished from the impact of zeolite framework on the structural and functional aspects of encapsulated guest metal complexes are in focus. To comprehend the effect of the extent of structural adaption of the guest metal complex and its correlation with the altered functionality of the encapsulated system, detailed characterization and theoretical studies have been carried out.

In the present work, square-planar Schiff- base complexes of different metals [Cu(II); d^9 , Co(II); d^7 , Pd(II); d^8 and Ni(II); d^8] have been synthesized via flexible ligand synthesis method, maintaining the molecular dimension or end to end distance in a series. Encapsulated systems are well characterized by the help of different characterization tools as well as theoretical studies to have better understanding of the host-guest systems. Electronic spectroscopy and magnetic studies are helpful to acquire the information about the structural alteration around the metal center. Ni(II) (d^8) Schiff-base complexes, as observed in the sixth chapter of the thesis, are diamagnetic in free-state but significant change in magnetic behavior of these systems is notified upon encapsulation in zeolite Y.

This thesis is included seven chapters where **chapter 1** describes a brief overview of the literature related to the present work and **chapter 2** includes experimental and characterization techniques which have been used to analyze the encapsulated systems and catalysis.

Chapter 3 of the thesis presents detailed studies of the nature of structural distortion of copper Schiff-base complexes undergone as a result of encapsulation in zeolite-Y and consequently, the modified structure enhance the reactivity and selectivity for the styrene oxidation reaction. To explore the extent of distortion, complexes with different molecular dimensions are entrapped within the voids of zeolite Y. The modified reactivity presented by the different encapsulated copper complexes evidently signify that the topology of the zeolite framework has profound influence on the structure of the encapsulated guest copper complexes and these copper complexes act significantly different in free-state and show substantial blue shifts in the d-d transition. Therefore the encapsulation of copper complexes actually alters the electronic properties of the complex via the steric hindered confinement.

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Chapter 4 of the thesis describes the studies related to the encapsulation of cobalt salophen complexes in zeolite Y. All free-state and encapsulated cobalt complexes are employed as catalysts for the degradation of Rhodamine B dye. On comparison with the free-state complexes, encapsulated cobalt systems are found far-more efficient catalysts and encapsulated cobalt complexes inside the supercages of zeolite probably facilitate the reaction by reducing the recombination of electron-hole pair and site isolation.

Chapter 5 of the thesis discloses the studies of palladium Schiff-base complexes encapsulated in zeolite-Y as catalysts for the Heck coupling reaction. This chapter reveals that the structural modification in the guest palladium complex plays a key role for the modified catalytic activity of the hybrid system towards Heck coupling. The observed red shift in metal-related transition evidently prove the alteration in the structure of guest Pd complex under encapsulation in zeolite Y which eventually enhances effective π -conjugation and hence increases the electron density around metal center and subsequently, zeolite encapsulated Pd complex is found more active as catalyst.

Pd complex with –OH substituents show aggregation with water molecules in its free-state via H-bonding whereas space constraint imposed by the zeolite supercage hinders such association of complexes. Therefore, comparative behavior of encapsulated Pd complex is strikingly different after encapsulation in zeolite-Y. Hence reactivity of encapsulated state is modified significantly upon encapsulation.

Chapter 6 of the thesis deals with the studies of two different series of Ni(II) salophen complexes [Ni(II) sal-1,2-phen and Ni(II) sal-1,3-phen series] in neat as well as in encapsulated states. The complexes of [Ni(II) sal-1,3-phen] series are proven to have non-planarity as compared to the [Ni(II) sal-1,2-phen] series in their free states and as a result, formation of more electropositive nickel center becomes the basis of the marginally better reactivity towards phenol oxidation. These observations are proved by the help of several spectroscopic techniques such as XRD, SEM-EDS, BET, XPS, IR, UV-vis studies and also thermal analysis and magnetic studies. The reason for the improved efficiency of the encapsulated Ni systems is administered by the modified coordination environment around metal center along with active site isolation inside the zeolite Y.

Chapter 7 of the thesis presents overall conclusion and future scope of current thesis work.