

ABSTRACT

Over the last two decades, the encapsulation of transition metal complexes within the voids of microporous zeolite has attracted attention of researchers since the material provides a simple way of coupling the reactivity of the metal complex with the robustness and stereochemistry of the host framework of zeolite. Transition metal Schiff-base complexes with suitable molecular dimensions and flexible ligands can be entrapped in the supercage of zeolite Y and these 'hybrid catalyst' are well known mimics of several biological enzymes such as cytochrome P-450, hemoglobin etc. A well explored area is the catalytic activity of the encapsulated complex which either enhances or is more selective as compared to the homogeneous counter parts. However comparatively fewer reports have offered 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 the adopted geometry and enhanced reactivity of such hybrid systems. 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 work of the thesis, the square-planar complexes of different transition metals [Ni(II); d^8 , Pd(II); d^8 , Co(II); d^7 and Cu(II); d^9] Schiff-base metal-salen and substituted metal salen complexes have been synthesized by flexible ligand synthesis approach, maintaining the increasing molecular dimension (average end-end distance) in a series. Encapsulated complexes are well characterized with the help of different techniques along with support of the theoretical studies. Magnetic studies and electronic spectroscopic studies are better platform to acquire information about the geometry around the metal-ion since Ni(II) (d^8) systems are diamagnetic in free state but have shown different behavior after encapsulation in zeolite Y. The Thesis is comprised seven chapters where chapter1 and chapter 2 include the introduction to the work and experimental and characterization techniques respectively.

Chapter 3 presents detailed studies of nickel Schiff-base complexes where the nature of geometry of the metal complex after encapsulation is studied by entrapping the same complex in different hosts (zeolite-Y and MCM-41) with cavities of different dimensions. To investigate the extent of distortion, complexes with different molecular dimensions are encapsulated in the same

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host zeolite Y. 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 entrapped complex for the styrene oxidation reaction in presence of H_2O_2 . Therefore the encapsulation actually modifies the electronic factors of the complex via the steric confinement.

In Chapter 4, encapsulation of palladium Schiff-base complexes in zeolite Y are explored. These complexes are well characterized and employed as catalysts for the sulfoxidation of methyl phenyl sulfide. On comparison with the neat states, encapsulated complexes are much better 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.

In Chapter 5, studies of copper Schiff-base complexes encapsulated in zeolite-Y as catalyst for the oxidation of styrene reveals that the alteration in the geometry of the complex plays a crucial role for the modified reactivity of the system. The observed shift towards higher binding energy in $Cu_{2p/3}$ (II) XPS signal for the encapsulated complexes is observed apparently indicating the generation more susceptible electropositive metal center for the nucleophilic attack. Therefore larger molecular dimension enforces more twist in geometry of complex and as an outcome; more susceptible metal center is generated for the nucleophilic attack.

In chapter 6, the study of square planar cobalt Schiff-base complexes in zeolite Y is presented. Alternation in adopted geometry is identified with the help of electronic spectroscopy and also magnetic behavior of the encapsulated complex. Encapsulation fabricates these complexes as better catalysts for degradation of rhodamine B since reactivity of the encapsulated complexes is mainly governed by extent of distortion upon encapsulation.

In chapter 7, overall conclusion and future scope present thesis work is discussed.



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