SYNOPSIS OF

METAL COMPLEXES IN CONSTRAINED ZEOLITIC ENVIRONMENTS – SYNTHESIS, CHARACTERIZATION AND PROPERTIES

A THESIS

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Introduction

Enzymes are catalyzing various oxidation reactions in regio- and stereo-controlled manner. They are catalyzing various electron transfer reactions in a logical sequence by using appropriate redox centers (Velde et al 2000). Enzymes which activate dioxygen to oxidize organic substrates into oxygenates are classified in to two groups according to the mode of oxygen incorporation. Dioxygenase incorporates two oxygen atoms whereas monooxygenase transfers only one-oxygen atoms. Iron, copper and manganese are most frequently found in the active centers of oxygenases. The active centers in the enzymes consist of metal complexes with nitrogen and oxygen containing chelating ligands (metal porphyrins, metal salen). Many synthetic complexes, which are having the same active sites as in the biological systems, are prepared. They are catalyzing various oxidation reactions as in biological system but they lose their catalytic activity in one cycle itself due to irreversible dimerization and irreversible oxidation of the ligands (Varkey et al, 1998, Sheldon et al 1998). Living systems have found a way to frustrate irreversible dimerization and destruction of ligands by encapsulating active sites in protein mantle. These protein mantles impose stearic constraints around a molecule from attacking other molecules. In order to increase the catalytic activity and stability of synthetic complexes, these complexes are encapsulated in various porous media and polymer matrices. Among the porous media zeolites are unique in the sense that the pore dimensions are not only uniform but also multidimensional in nature (Viswanathan 1996). The complexes are stabilized inside the zeolite due to two factors. In the appropriate zeolite host the molecule is free to move about with in the cavities of the zeolite but prevented from leaching by restrictive pore openings (ship in a bottle) (Balkus 1996)

Interaction of certain functional groups of the complexes with some species on the walls of the zeolites, which bind the metal complexes to the zeolites (host-guest interaction). This will prevent irreversible dimerization and destruction of the ligands. Metal complexes encapsulated in zeolites can mimic metalloenzymes and can therefore be termed as zeozymes (Armengol et al 1999, Jacob et al 1998).

Motivation and scope of the investigation.

Though there have been several reports on encapsulation of transition metal complexes in various zeolites, there are certain questions, which is not answered in the literature.

1. When metal complexes are encapsulated in various zeolites, the redox potential of the metal complex is altered. The reason for the alteration of redox potential of the metal complexes is not clear in the literature (Briot et al 1998, Jiang et al 2000).

2. The natural systems are carrying out various oxidation reactions in a selective manner by adjusting the redox potential of metal complexes in various protein mantles (W.M.Clark 1960). Similar type systems can be generated by encapsulating same metal complexes in various zeolites. By knowing the redox potential of metal complexes in various zeolites one can choose an appropriate system for a particular reaction. Attention has not been paid in the literature to generate such type of systems using encapsulation of metal complexes in zeolites

3. The HOMO and LUMO of metal complex is altered in various zeolites. These alteration changes all the properties of metal complexes in various zeolites. In the literature attention has not been paid to calculate HOMO and LUMO level of metal complexes theoretically

With this in mind, transition metal complexes are encapsulated in various zeolites. The scope of the present investigation thus includes:

1. Encapsulation of copper ethylenediamine $(Cu (NH_2CH_2CH_2NH_2)_2)^{2+}$(Cu-en), Copper 8-hydroxy quinoline $(Cu(C_9H_6NO)_2)$ (Cu-Qn)] (Cu-Qn), Manganese 8-hydroxy quinoline $(Mn(C_9H_6NO)_2)$ (Mn-Qn), Ferroin (Fe $(phen)_3^{2+}$) Binuclear iron 1,10 phenanthroline $(Fe_2O(phen)_4Cl_4.6H_2O)$ (Fe-Phen), Cobalt dimethyl glyoxime $(Co(dmg)_2)$ complexes in various zeolites (NaY, KL, Naβ, NaZSM-5, MCM-41).

2. Physico-chemical characterization of the synthesized materials by XRD, FT-IR, Thermal analysis, UV-Vis, ESR.

3. Study of redox potential of metal complexes in neat and encapsulated system by cyclic voltammetry.

4. Theoretical calculation of HOMO and LUMO level of metal complexes by Density Functional Theory(DFT)

5. Immobilization of cytochrome-C and Vitamin B_{12} on MCM-41 materials.

6. Catalytic activity of encapsulated complexes towards oxidation of various substrates (cyclohexanol, benzyl alcohol, dimethyl sulfide) and comparison with biological systems.

Experimental techniques.

Appropriate metal salts(Table 1) (0.1M) are exchanged with various zeolites and heated with excess ligands. The resulting materials are soxhlet extracted with various solvents to remove the loosely bound metal complex and excess ligand present on the surface. The experimental parameters are given in Table1. Cytochrome-C was immobilized by adding 5ml of 150μM cytochrome-C solution in phosphate buffer

(pH=6.0) to 100 mg of MCM-41. The mixture was then stirred for 2h in an ice bath [24].

The supernatant liquid was separated from the solid material by centrifugation.

The amount of immobilized enzyme was calculated from the difference in absorbance of supernatant liquid at 409.6 nm before and after addition of the support. The cytochrome-C immobilized in MCM-41 was washed with de-ionized water and air-dried. The Vitamin B_{12} was immobilized in MCM-41 materials at pH 9 using the same procedure employed for cytichrome-C.

Table 1. Experimental parameters involved in encapsulation of metal complexes

M	L	Metal salts	Temp (K)	Solvent	Zeolite	Atmosphere
Cu (II)	Ethylenediamine	Copper nitrate	303	Water	NaY, KL, MCM-41, Naβ, NaZSM-5	Air
Cu (II)	8-Hydroxyquinoline	Copper nitrate	393	Acetone	NaY, KL, MCM-41, Naβ, NaZSM-5	Air
Mn(II)	8-Hydroxyquinoline	Manganese acetate	473	Acetone	NaY, KL, MCM-41, Naβ, NaZSM-5	Argon
Co(II)	Dimethylglyoxime	Cobalt nitrate	303	Water	NaY, KL, MCM-41, Naβ, NaZSM-5	Argon
Fe(II)	1, 10 Phenanthroline	Ferrous Ammonium sulphate	303	Acetonirile	MCM-41	Argon
Fe(III)	1,10 Phenanthroline	Ferrous ammonium sulphate	393	Acetonirile	MCM-41,	Air

To study the structure of the zeolite before and after encapsulation of metal complexes XRD technique was used. To know the geometry of the metal complex before and after encapsulation of metal complexes and bonding nature of the metal complex was studied by IR , UV-Vis, and EPR measurements. The redox potential of metal complex was studied using cyclicvoltammetry.

Liquid phase oxidation of cyclohexanol and benzyl alcohol and Dimethyl sulfide was carried out at room temperature using hydrogen peroxide and tertiary butylperoxide as oxidant. In all the cases, product identification was done with GC-MS and quantitative analysis of the products was made by gas chromatography.

Computational details.

The DFT calculations were carried out using the Gaussian 98 program. All DFT calculations were done by Becke three parameter hybrids functional with the LYP correlation function (B3LYP) [26] and an effective core potential basis set LanL2DZ [27]. Clusters of ten (Si10O10H20)(D10h symmetry) and twelve (Si12O12H24)(D12h symmetry) membered ring systems with 40 and 48 atoms respectively were used for the simulations, where the residual valence of silicon atoms were saturated with hydrogen atoms. The optimization of geometry was obtained by using universal force field approach (UFF1.02). In a typical calculation method, the metal complex was placed at the center of ten (Si10) and twelve (Si12) membered ring systems and geometry was optimized by universal force field approach. Cerius2 software was used for force field calculations. Using force field optimized parameters DFT calculations were done at B3LYP/LanL2DZ level. Similar procedure was used to obtain force field optimized geometries with different heteroatom (B, Al, Ga) substituted clusters.

Results and Discussion.

The XRD pattern of zeolite before and after encapsulation of metal complexes is similar. It suggests that zeolite retains its crystalline structure after encapsulation. The IR spectra are recorded after encapsulation of metal complexes (fig 2). Same band is observed after encapsulation of metal complexes. It suggests that same metal complex is formed inside the zeolite matrix. In the case of copper ethylenediamine the N-H $_{def}$ band is shifted towards

lower wave numbers upon encapsulation. It indicates that Cu-en is interacting with zeolite matrix. In the case of copper 8-hydroxyquinoline, the C=C and C=N stretching frequency is shifted towards lower wave numbers upon encapsulation in zeolite matrices. There is no change in the position of band for Mn-Qn and Fe-phen complexes upon encapsulation. The UV-Vis band of Cu-en (d-d transitition) is blue shifted in the case of NaY and red shifted in the case of beta, KL and ZSM-5 zeolites. Similar trend is observed in the case of Cu-Qn complexes ($\pi \rightarrow \pi^*$). In the case of Mn-Qn complexes, the band ($\pi \rightarrow \pi^*$) is blue shifted in all zeolites after encapsulation. This suggests that molecule is not having same geometry as in the neat complex but undergoes distortion in various zeolites. EPR spectra for neat and encapsulated complexes were recorded at liquid nitrogen temperature (LNT). The slight deviation in g and A values is due to axial distortion of metal complexes in various zeolites.

The redox properties were studied using cyclic voltammetry. Peaks are getting broadened and different electrochemical responses were observed after encapsulation of metal complexes (Fig 1). This indicates that metal complex is having different redox potential at different places of zeolites. This may be due to heterogeneous nature of zeolite surfaces. Because of the zeolite geometry, cages, channels, side packets and charge distribution, field gradients exists.   This may alter the energy levels of the metal complex so that metal complexes present at different locations of zeolite have altered redox potentials. Peak potential are getting shifted towards more positive values upon encapsulation of Cu-Qn and Mn-Qn complexes in various zeolites. This indicates that metal complexes are having higher oxidizing power compared to that of neat complex. As in the biological enzymes, redox potential of same metal complex is shifted when it is encapsulated in different zeolites (fig 3).   Redox potential is altered both in biological systems as well as in zeozymes. In order to compare zeozymes with biological systems, cytochrome-C and vitamin B_{12} has been

immobilized in MCM-41.   The electrochemical data for neat and encapsulated cytochrome-C and vitamin B_{12} are given in Table 2. As in the zeozymes the redox potential is altered towards more positive value upon encapsulation in MCM-41.

Table 2 redox properties of neat and immobilized biological systems

Catalyst	E_{pa}	E_{pc}	$E_{1/2}$
Cytochrome-C	93	26	59.5
Cytochrome-C/MCM-41	150	110	130
Cytochrome-C/MCM-48	170	130	150
Vitamin B_{12}	-790	-958	---
Vitamin B_{12}/MCM-41	-791	-841	-816

Theoretical methods.

These are the following observations from physio chemical characterization of metal complexes

- Change in the λ_{max} of metal complexes upon encapsulation-blue or red shifted – depends upon the zeolite.

- Peak potential altered upon encapsulation.

- Change in the position of HOMO and LUMO level of metal complexes upon encapsulation.

In order to calculate the position of HOMO and LUMO level of metal complexes in various zeolites, DFT theory was used. After encapsulation of metal complexes in ten and twelve membered ring systems, the bond length decreases (Table 3) and molecule deviates from squire planarity.   This may be due to repulsion between electrons in the metal complex and walls of the zeolites. The HOMO and LUMO level of metal complex

increase upon encapsulation in ten and twelve membered ring systems (Table 4). . In the case of encapsulated complexes HOMO and LUMO were considered which has main contribution from metal complexes (Table 5). The type of interaction normally considered when the metal complex is encapsulated inside the zeolite is the following

(i) Columbic effects: these are produced by the charge distribution along the framework owing to the partial ionic character of the ionic crystals. This charge distribution generates strong columbic field on the cavities, which might alter the energy level of metal complexes as well as influence the chemical behavior of the transition metal complexes.

(ii) Coordination effects. These are produced by Lewis acid-base type interactions among the transition metal complexes and certain sites of the frame work in the cavity. Weak electron interactions account for the forces of van der Walls type.

 (iii) Double layer effect. Zeolite framework is anionic in nature. When the transition metal complex enters the zeolite cavity it forms a double layer in the zeolite cavities. It is known in the literature that electric field existing in between a double layer is around 108V/cm. This electric field alters the energy levels as well as chemical behavior of the transition metal complexes.

Table 3. Optimized parameters for neat and encapsulated complexes.

Catalyst	Cu-O1	Cu-N1	Cu-O2	Cu-N2	<N1-Cu-O1	<N2-Cu-O2	<N2-Cu-O1	<N1-Cu-O2
Cu-Qn-XRD	1.93	1.97	1.93	1.97	84.50	84.80	94.90	95.80
Cu-Qn DFT OPT	1.96a	1.98	1.96	1.98	84.62b	84.62	95.37	95.37
Cu-Qn-UFF OPT	1.92	1.96	1.92	1.96	86.91	86.91	93.09	93.09
Cu-Qn-Water	2.01	2.01	2.01	2.01	83.78	83.78	96.21	96.21
Cu-Qn-Si10	1.86	1.89	1.86	1.89	94.96	94.96	117.05	117.05
Cu-Qn- AlSi10	1.86	1.90	1.86	1.90	94.74	94.71	116.97	118.73
Cu-Qn- Si12	1.87	1.88	1.87	1.88	95.58	95.58	117.42	117.42
Cu-Qn- AlSi12	1.87	1.88	1.87	1.88	95.65	95.65	117.18	117.18
Cu-Qn- BSi12	1.86	1.88	1.86	1.88	95.61	95.61	117.55	117.68
Cu-Qn- GaSi12	1.86	1.88	1.86	1.88	95.63	95.63	117.07	118.12

Distance in angstroms, Angle in degrees.

Upon substitution of heteroatoms the HOMO and LUMO level gets stabilized. This may be due to decrease of electric field inside the zeolites by charge compensating protons.

Table 4 the HOMO and LUMO values for neat and encapsulated Cu-Qn complexes

Catalyst	HOMO (eV)	LUMO (eV)
Cu-Qn-DFTOPT	-5.36	-2.09
Cu-Qn-UFFOPT	-5.29	-2.15
Cu-Qn-Water	-4.87	-1.51
Cu-Qn-Si10	-4.86	-1.69
Cu-Qn- AlSi10	-5.21	-2.11
Cu-Qn- Si12	-4.88	-1.61
Cu-Qn- AlSi12	-5.08	-1.98
Cu-Qn- BSi12	-5.03	-1.96
Cu-Qn- GaSi12	-5.14	-2.11

Table 5   Percentage atomic orbital contributions to HOMO and LUMO level of Cu-Qn and Cu-Qn-Si12

Catalyst	Si		Ozeo		Hzeo	Cu			Ocomplex		N		C		Hcom
	s	p	s	p	s	s	p	d	s	p	s	p	s	p	s
Cu-Qn HOMO -5.36 eV	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.97	0.00	31.35	0.00	2.85	0.00	63.83	0.00
LUMO -2.09 eV	0.00	0.00	0.00	0.00	0.00	0.00	2.26	0.00	0.00	0.91	0.00	20.03	0.00	76.80	0.00
Cu-Qn-Si12 HOMO -4.88 eV	0.13	0.30	0.09	0.24	0.10	0.00	0.38	8.85	0.09	32.83	0.71	4.35	1.44	50.42	0.07
LUMO -1.61 eV	0.31	0.65	0.20	0.66	0.24	0.09	0.42	1.06	0.05	2.36	0.08	21.60	0.26	71.96	0.06

Catalytic activity.

The liquid phase oxidation of cyclohexanol was carried out using neat and encapsulated Mn-Qn complexes (Table 5). TON increases twenty seven to thirty six times upon encapsulation of metal complexes. All other catalysts are not active for oxidation of cyclohexanol.   This may be due to alteration of redox potential of metal complexes in various zeolites.   Because of this, Mn-Qn complex encapsulated in NaY and KL zeolites are active for liquid phase oxidation of cyclohexanol.

Table 6. Catalytic activity towards oxidation of cyclohexanol by neat and encapsulated
Mn- Qn complexes

Catalyst	Conversion Cyclohexanone (Mole %)	TON
Mn-Qn	20.0	15
Mn-Qn-NaY	21.4	399
Mn-Qn-KL	23.5	564

Conditions: Weight of the catalyst=100mg, Cyclohexanol:H_2O_2=1:1, Temperature=307K

Liquid phase oxidation of benzyl alcohol is carried out using neat and encapsulated Fe-phen complexes. neat complex is showing lesser activity due to cleavage of Fe-O-Fe bridge but in encapsulated system it is stable(Table 7).

Table 7. Catalytic activity towards oxidation of benzyl alcohol by neat and encapsulated Fe-phen complexes

Catalyst	Conversion Benzaldehyde (mole %)	TON
Fe-phen	7.1	80
Fe-phen-MCM-41	34.9	1041
Fe-phen-MCM-41 (First reuse)	23.3	989

Liquid phase oxidation of dimethyl sulfide was carried out using neat and encapsulated Cu-en complexes at room temperature. Neat is inactive for the oxidation of dimethyl sulfide. Upon encapsulation in various zeolites it is showing higher activity. This may be due to site isolation of copper ethylenediamine complexes in constrained environment. Similar reaction was compared with cytochrome-C. Cytochrome-C alone is inactive for the oxidation of dimethyl sulfide. Upon immobilization it is giving 97.8% conversion.

Table 8 Catalytic activities towards oxidation of dimethylsulfide by neat and
encapsulated Cu-en complexes

Catalyst	Conversion Dimethyl sulfoxide Mole(%)	TON
Cu-en	0	0
Cu-en-NaY	75.1	466
Cu-en-KL	99.3	1383
Cu-en-Naβ	95.0	1050
Cu-en-ZSM-5	98.8	1597
Cu-en-MCM-41	81.3	1313
Cytochrome-C	0.0	0.0
Cytochrome-C/MCM-41	97.8	10000

Conclusions:

- Copper, manganese and iron metal complexes which are having same active
  centers(metal with chelating ligands) as in the biological systems are encapsulated
  in various zeolites(NaY,KL,Naβ, NaZSM-5, MCM-41).
- IR spectra confirms the formation of metal complexes inside the zeolite matrix
- UV-Vis and EPR spectra show that geometry of the metal complexes change and
  metal complexes undergo axial distortion inside the zeolite matrix.
- Cyclic voltammetry studies show that redox potential of metal complex is altered
  inside the zeolite matrix. It confirms that metal complex located at different
  places of the zeolite matrix is having different redox potentials. These properties

were rationalized using physical properties of the zeolite matrix. Redox potential of biological is also altered as in the zeozymes when it is mobilized on mesoporous materials.

- Theoretical calculations show that decrease of bond length between metal and ligands upon encapsulation of metal complexes in ten and twelve membered ring systems. The HOMO and LUMO level of metal complex increase upon encapsulation. Upon substitution in ten and twelve membered ring system it gets stabilized.

- In the oxidation of cyclohexanol, Mn-Qn complex encapsulated in NaY, and KL zeolites are showing higher activity. All other Mn-Qn catalysts are not showing any activity.

- Fe-O-Fe bridge in neat complex gets cleaved in the oxidation of benzyl alcohol but it gets stabilized upon encapsulation in MCM-41.

- Cu-en and cytochrome-c are not showing any activity but activity increases enormously upon encapsulation in zeolite and mesoporous materials.

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Proposed contents of the thesis

Chapter 1.   **Introduction**

Chapter 2.   **Experimental Methods**

Chapter 3.   **Synthesis, characterization of metal complexes encapsulated in various zeolites**

Chapter 4.   **Theoretical methods**

Chapter 5.   **Catalytic activity of metal complexes encapsulated in various zeolites**

Chapter 6.   **Summary and conclusions.**

Refereed journals

1. **R.Ganesan and B.Viswanathan** (2000) Encapsulation of metal complexes in zeolites-possible mimics for natural enzymes. *Bull.Catal.Soc*(India) 10, 1.

2. **R.Ganesan and B. Viswanathan (2002***)* Synthesis, characterization and catalytic activity of μ- oxo bridged dinuclear iron 1,10 phenanthroline complex encapsulated in MCM-41 J.Mol.Catal, 181, *99.*

3. **R.Ganesan and B. Viswanathan** *(* 2001) Redox properties of metal complexes in various zeolites *Indian J.Chem, ,* 49A, 255.

4. **R.Ganesan, and B. Viswanathan** (2003) Redox properties of copper oxinate complex in various zeolites.*Bull.Catal.Soc(India)* 2(1&2), 1.

5. **R.Ganesan and B. Viswanathan** Redox properties of bis(8-hydroxyquinoline)Manganese(II) encapsulated in various zeolites J.Mol.Catal (in press)
.
6. **R.Ganesan and B. Viswanathan** Redox properties of bis(8-hydroxyquinoline)Copper(II) encapsulated in various zeolites *Catal.Today (To be communicated)*

7. **R.Ganesan and B. Viswanathan** On the analogy of encapsulated complexes (zeozymes) with enzyme mimics in protected environments. *(To be communicated*)

In National/International Conference

1. **R.Ganesan and B. Viswanathan,** Synthesis, characterization and catalytic activity of μ-oxo bridged dinuclear iron 1,10 phenanthroline complex encapsulated in MCM-41. Presented in Catalysis Symposium-15 (CATSYMP-15) and Indo-Pacific catalysis Association (IPCAT-2) at Pune, Jan 23rd-25th 2001.

2. **R.Ganesan and B.Viswanathan,** Synthesis, characterization of copper ethylinediamine complex encapsulated in various zeolites. Presented in National Workshop on Catalysis (Catwork-2002) held at Department of chemistry, Gauhati university, Gauhati Mar 8th –10th 2002.

3. **R.Ganesan and B.Viswanathan,** Redox properties of bis(8-hydroxyquinoline)manganese(II) encapsulated in various zeolites.
Presented in 16th National Symposium On Catalysis and First Indo-German Conference on Catalysis held at Indian Institute of Chemical technology, Hyderabad Feb 6th –8th *2003.*