

Zeolite-encapsulated Co(II), Ni(II) and Cu(II) complexes as catalysts for partial oxidation of benzyl alcohol and ethylbenzene

K.O. Xavier^{a,1}, J. Chacko^a, K.K. Mohammed Yusuff^{b,*}

^a Department of Chemical Oceanography, Cochin University of Science and Technology, Cochin 682 022, India

^b Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682 022, India

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Abstract

Co(II), Ni(II) and Cu(II) complexes of dimethylglyoxime and *N,N'*-ethylenebis(7-methylsalicylideneamine) have been synthesized in situ in Y zeolite by the reaction of ion-exchanged metal ions with the flexible ligand molecules that had diffused into the cavities. The hybrid materials obtained have been characterized by elemental analysis, SEM, XRD, surface area, pore volume, magnetic moment, FTIR, UV-Vis and EPR techniques. Analysis of data indicates the formation of complexes in the pores without affecting the zeolite framework structure, the absence of any extraneous species and the geometry of encapsulated complexes. The catalytic activities for hydrogen peroxide decomposition and oxidation of benzyl alcohol and ethylbenzene of zeolite complexes are reported. Zeolite Cu(II) complexes were found to be more active than the corresponding Co(II) and Ni(II) complexes for oxidation reactions. The catalytic properties of the complexes are influenced by their geometry and by the steric environment of the active sites. Zeolite complexes are stable enough to be reused and are suitable to be utilized as partial oxidation catalysts.

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1. Introduction

Transition metal complex-catalyzed oxidation of organic compounds is a field that has been extensively investigated in the past [1,2]. Although homogeneous catalysts exhibit excellent activity and selectivity, the technical problems encountered in their applications, such as the difficulty in product separation and the deactivation by self-aggregation of active sites, have slowed their industrial applications. In the search to minimize these disadvantages, the heterogenization of homogeneous catalysts has emerged as a focus of research. Several polymer and inorganic oxide-anchored complexes have been developed with catalytic activities as good as those of homogeneous complexes [3,4]. However, some disadvantages like leaching of metal complexes from

the solid surface restrict their commercial usage. Encapsulation in microporous solids such as zeolite is an attractive technique for heterogenization, since no leaching is observed when the complex is confined exclusively in the zeolite pores [5]. In addition, zeolite-encapsulated complexes promise better control of selectivity of the reaction and higher stability due to the reduced dimerization of complexes in the cavity [6]. Furthermore, these systems have attracted attention in biomimetic chemistry as models of enzyme active centers in which the zeolite framework represents a rigid protein mantle [7].

Significant progresses are made in the design and synthesis of zeolite-encapsulated complexes for catalytic applications [8,9]. Most of such catalysts synthesized were based on ligand systems like ethylenediamine [10], bipyridine [11], salen [12] and phthalocyanines [13]. Interestingly, subsequent studies on these encapsulated complexes have shown their unique reactivity for many industrially important reactions. For example, encapsulated salen complexes have been successfully employed for epoxidation [14], oxidation of phenols [15], direct oxidation of methane to methanol [16] and oxidation of *p*-xylene to terephthalic acid [17]. Simi-

* Corresponding author. Tel.: +91-484-2575804; fax: +91-484-2577595.

E-mail addresses: koxavier@yahoo.com (K.O. Xavier), yusuff@cusat.ac.in (K.K. Mohammed Yusuff).

¹ Present address: Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel.

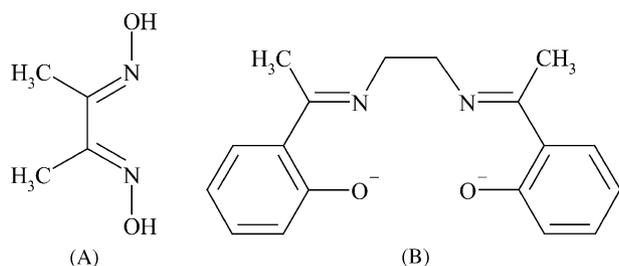


Fig. 1. Structure of: (A) dmgH_2 and (B) Me_2salen .

larly, encapsulated phthalocyanine complexes are known to promote the oxidation of hydrocarbons that mimic metalloenzymes [18], direct synthesis of adipic acid from cyclohexane or cyclohexene [19] and oxyhalogenation of aromatics [20]. Recently, we have reported Y zeolite-encapsulated complexes of 3-formylsalicylic acid as catalysts for oxidation reactions [21]. The recent spurt of literature on encapsulated catalysts shows the growing current interest in exploring zeolite complexes of new ligand systems for structural and catalytic studies.

Intrazeolite transition metal complexes of dimethylglyoxime (dmgH_2) were synthesized previously for spectral studies [22,23]. Although the simple Co(II) complex of dmgH_2 is known to activate molecular oxygen and catalyze oxidation reactions [24], encapsulated dmgH_2 complexes of neither Co(II) nor other metal ions have been thoroughly investigated for catalytic activity [25,26]. Another important ligand system whose encapsulated complexes have been rarely studied is salen analogues like *N,N'*-ethylenebis(7-methylsalicylideneamine) (Me_2salen). Herein, we report the synthesis, characterization and catalytic activities of Y zeolite-encapsulated Co(II), Ni(II) and Cu(II) complexes of dmgH_2 and Me_2salen ligands (Fig. 1). The synthetic approach employed by us is a two-stage process called the flexible ligand method [27]: (i) ion-exchange of metal ions into zeolite, and (ii) complexation of metal ions with ligand molecules diffused into the supercage. Zeolite complexes were characterized by chemical analysis, morphological and surface techniques (XRD, SEM, surface area and pore volume), magnetic moment and spectroscopic techniques (FTIR, UV-Vis and EPR). The data are interpreted to indicate the encapsulation of complexes and to assign tentatively their structure and geometry. The complexes were screened for catalytic activities of hydrogen peroxide decomposition and the oxidation of benzyl alcohol and ethylbenzene.

2. Experimental

2.1. Materials

Metal chloride salts, dimethylglyoxime, 2-hydroxyacetophenone, ethylenediamine, hydrogen peroxide, benzyl alcohol and ethylbenzene were from Merck (GR grade).

Dimethylglyoxime was further purified by recrystallization from ethanol. The ligand, Me_2salen , was synthesized by the condensation of 2-hydroxyacetophenone with ethylenediamine as reported earlier [28]. The sodium form of Y zeolite (YNa) obtained from Süd-Chemie, India, was dried at 723 K for 4 h prior to being used as the host material for encapsulating complexes. Metal-exchanged Y zeolites are designated as YM and zeolite complexes as YML_n (M: metal ion, L: ligand, $n = 1$ for Me_2salen or 2 for dmgH_2).

2.2. Synthesis of complexes in Y zeolite

YNa zeolite was ion-exchanged with 0.007 M metal chloride solution at 363 K for 8 h and then dehydrated at 673 K for 4 h to obtain YCo, YNi and YCu zeolites. The anhydrous metal-exchanged zeolite was mixed with an excess of dmgH_2 or Me_2salen . These solids were heated in sealed glass ampoules for a period of 16 h at 363 K in the case of dmgH_2 samples and at 423 K for Me_2salen samples, to effect complexation. The resultant mass, except in the case of $\text{YNi}(\text{dmgH})_2$, was Soxhlet-extracted with methanol to remove surface complexes and the free ligand. $\text{YNi}(\text{dmgH})_2$ was purified by extracting with chloroform and then with methanol. The extraction in each case was continued for 16 h after the extracting solvent became colorless. The purified sample was ion-exchanged with 0.1 M NaCl for 24 h to remove uncomplexed metal ions from the lattice. The zeolite complex thus obtained was filtered, washed free of chloride ions and then dried in vacuum.

2.3. Catalyst characterization

2.3.1. Elemental analysis

A known weight of the anhydrous sample was treated with sulfuric acid and then with hydrofluoric acid. The solution was evaporated to remove silicon as SiF_6 . The loss in weight corresponds to the amount of silica present in the sample. The residue obtained was fused with potassium pyrosulfate and then dissolved in a known volume of water. This solution was analyzed for metal contents using a Perkin Elmer-3110 atomic absorption spectrophotometer. The C, H and N contents of the samples were analyzed using a HER-AEUS elemental analyzer.

2.3.2. Physical techniques

X-ray powder diffraction patterns were recorded using a Rigaku D-max III, X-ray diffractometer with Ni filtered $\text{Cu K}\alpha$ radiation. Scanning electron micrographs were recorded on a Leica Stereoscan-440. A Micromeritics Gemini-2360 was used for measuring surface area and pore volume of the samples by nitrogen adsorption at different relative pressures in the range 0.1–0.9 at liquid nitrogen temperature. Prior to adsorption measurement, the samples were dried at 373 K in a stream of nitrogen for 3 h and then degassed at 303 K. The surface area was computed from the volume of adsorbed gas for monolayer coverage as per the BET

method. The pore volume of the samples is given by the volume of liquid nitrogen equivalent to the nitrogen gas adsorbed at a relative pressure of 0.9. The magnetic moment was measured at 303 K using the Guoy method. Infrared spectra in the region $400\text{--}4600\text{ cm}^{-1}$ were recorded in KBr pellets using a Shimadzu 8101 FTIR spectrophotometer. The spectrum obtained after multiple scans was a plot of percentage transmittance against wave number. A Cary Win UV-Vis spectrophotometer was used for recording diffuse reflectance spectra in the range $200\text{--}2000\text{ nm}$, using MgO as reference. The reflectance data were represented as a plot of the Kubelka–Munk function, $F(R) = (1 - R)^2/2R$, against wavelength. EPR spectra of Cu(II) complexes were recorded using a Varian E-109 X/Q bands spectrophotometer and g values were estimated relative to tetracyanoethylene.

2.4. Catalytic activity

2.4.1. Decomposition of hydrogen peroxide

Fifty milligram of the catalyst sample was stirred in hydrogen peroxide solution (30 ml, 30% aqueous) at 303 K. The volume of oxygen gas liberated was measured using a gas burette attached to the reaction flask and plotted against time.

2.4.2. Catalytic oxidation reaction

The oxidation reaction was performed in a reaction flask of 100 ml capacity equipped with a reflux condenser. The flask was maintained at the specified reaction temperature using an electrically heated oil bath. The substrate, benzyl alcohol (3.24 g, 0.03 mol) or ethylbenzene (3.18 g, 0.03 mol), was dissolved in 10 ml benzene and mixed with 50 mg of catalyst sample in the flask. Hydrogen peroxide (2.04 g, 0.06 mol; 30%, w/v) was added and the mixture was stirred magnetically for 8 h. The unreacted substrate and product obtained were analyzed using a Chemito 8310 Gas Chromatograph with SE 30 column and FID detector.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) and X-ray diffraction (XRD)

Encapsulation of Co(II), Ni(II) and Cu(II) complexes of dmgH_2 and Me_2salen ligands in Y zeolite was accomplished using a flexible ligand synthesis scheme. The ligands, which are flexible enough to diffuse through the zeolite channels, react with the pre-exchanged metal ions in the supercage to afford the encapsulated complexes. The product material was purified by extensive soxhlet-extraction with suitable solvents to remove unreacted ligand and surface complexes, and then by NaCl treatment to re-exchange free metal ions from the zeolite lattice. The samples did not change their color on purification, indicating that the complexation has occurred in the cavities and that the resulting complexes are too large to diffuse out of zeolite through the channels. SE micrographs of $\text{YCu}(\text{dmgH})_2$ taken before and after purification are shown in Fig. 2 as a representative case. In the SEM taken before purification, the complexes deposited on the external surface are visible. In the SEM of finished products, no surface complexes are seen and the particle boundaries on the external surface of zeolite are clearly distinguishable. These micrographs reveal the efficiency of purification procedure to effect complete removal of extraneous complexes, leading to well-defined encapsulation in the cavity [29]. Analysis of XRD patterns indicates that the metal-exchanged zeolites and zeolite complexes have crystallinity almost identical to that of the parent YNa zeolite. It appears that metal exchange and encapsulation conditions have little impact on the crystallinity of zeolite host [29]. Moreover, no crystalline patterns were seen for the encapsulated complexes; this might be because of their fine distribution in the lattice.

3.2. Analytical results

The analytical data of host zeolites and zeolite complexes are given in Table 1. The parent YNa zeolite has a Si/Al

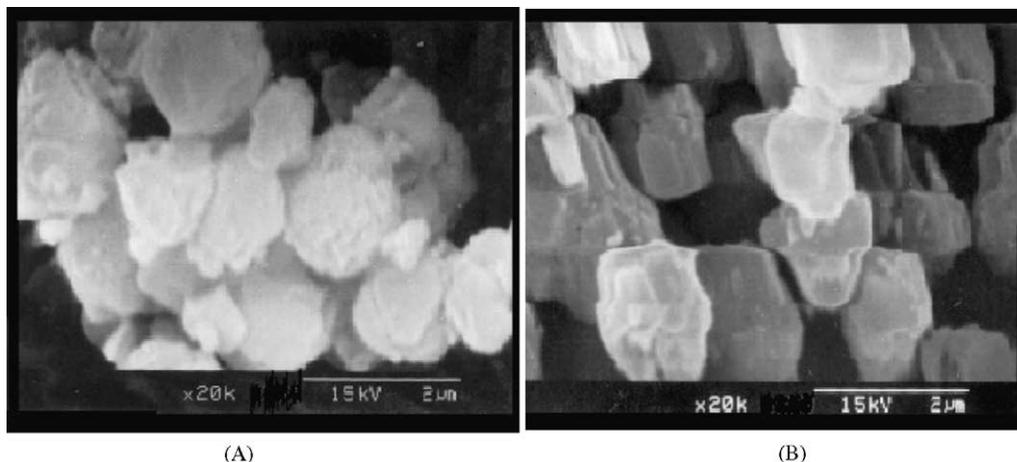


Fig. 2. SE micrographs of $\text{YCu}(\text{dmgH})_2$ before (A) and after (B) soxhlet-extraction.

Table 1
Analytical data and unit cell formulae

Sample	Metal (%)	Si (%)	Al (%)	Na (%)	C (%)	H (%)	N (%)	Unit cell formula
YNa		21.76	8.60	7.50				Na ₅₆ [(AlO ₂) ₅₆ (SiO ₂) ₁₃₆]
YCo	3.64	21.53	8.52	3.35				Na ₃₄ Co ₁₁ [(AlO ₂) ₅₆ (SiO ₂) ₁₃₆]
YCo(dmgh) ₂	1.78	19.45	7.71	6.56	2.77	0.46	1.62	
YCoMe ₂ salen	1.85	19.45	7.67	6.82	6.03	0.51	0.78	
YNi	3.72	21.79	8.62	3.28				Na _{33.8} Ni _{11.1} [(AlO ₂) ₅₆ (SiO ₂) ₁₃₆]
YNi(dmgh) ₂	1.63	19.48	7.70	6.15	2.59	0.43	1.50	
YNiMe ₂ salen	2.78	19.40	7.68	5.25	8.39	0.71	1.09	
YCu	3.86	21.48	8.48	3.12				Na _{34.4} Cu _{10.8} [(AlO ₂) ₅₆ (SiO ₂) ₁₃₆]
YCu(dmgh) ₂	1.58	19.44	7.68	6.30	2.30	0.38	1.33	
YCuMe ₂ salen	1.61	19.43	7.67	6.30	4.76	0.40	0.62	

molar ratio of 2.4, which corresponds to a unit cell formula Na₅₆[(AlO₂)₅₆(SiO₂)₁₃₆]. The Si/Al ratio has remained unchanged in all metal-exchanged zeolites, indicating the absence of dealumination during ion-exchange. Initial metal loading in zeolite lattice is in the range 3.6–3.9%, whereas the metal contents are considerably lower in zeolite complexes. This decrease in metal contents could be partly attributed to the formation of complexes inside the cavities. The unreacted metal ions in the lattice are expected to be re-exchanged in the final NaCl treatment. The metal, C, H and N contents indicate a ligand/metal molar ratio of around 2 for dmgh₂ complexes and 1 for Me₂salen complexes. However, the slightly lower molar ratio in each case indicates the presence of minute traces of free metal ions in the lattice. These free metal ions which could not be re-exchanged due to the shielding by the guest molecules are not expected to cause any serious interference in the behavior of encapsulated complexes [25].

3.3. Surface area and pore volume

Surface area and pore volume of zeolites and zeolite complexes are given in Table 2. The adsorption isotherms are typical of microporous solids in the case of both parent YNa and modified zeolites. Negligible loss of surface area or pore volume is observed on metal-exchange in zeolites, whereas the values are reduced considerably for zeolite complexes.

Table 2
Surface area and pore volume data

Sample	Surface area (m ² /g)	Pore volume (ml/g)
YNa	545	0.30
YCo	532	0.30
YCo(dmgh) ₂	375	0.23
YCoMe ₂ salen	269	0.17
YNi	528	0.30
YNi(dmgh) ₂	232	0.14
YNiMe ₂ salen	260	0.17
YCu	534	0.30
YCu(dmgh) ₂	344	0.22
YCuMe ₂ salen	389	0.24

Since the zeolite crystallinity is retained, such lowering of surface area and pore volume is a direct evidence for the presence of complexes in the cavities. A similar reduction of surface area was observed in the case of encapsulated salen and phthalocyanine complexes by previous workers [29,30]. Surface area of zeolite complexes is obviously greater than the geometrical surface of the zeolite crystal as a result of the nitrogen uptake by internal surfaces. Thus the internal surface is only partially blocked by the encapsulated complexes.

3.4. FTIR spectroscopy

IR spectra of YNa and metal-exchanged zeolites show strong zeolite lattice bands in the range 450–1200 cm⁻¹. The strong and broad band at the region 1000 cm⁻¹ could be attributed to the asymmetric stretching vibrations of (Si/Al)O₄ units. The broad bands at the region 1650 and 3500 cm⁻¹ are due to lattice water molecules and surface hydroxylic groups. IR spectra of encapsulated complexes are presented in Fig. 3. No shift of zeolite lattice bands is observed in the spectra of encapsulated complexes, which further implies that the zeolite framework has remained unchanged upon the encapsulation of complexes. The coordination in the pores could be identified from the bands observed in the region 1200–1600 cm⁻¹ where zeolite has no bands. However, the bands due to complexes are weakly intense due to their low concentrations in the lattice. The νC=N observed at 1620 cm⁻¹ in the spectrum of free dmgh₂ has shifted to 1599, 1572 and 1595 cm⁻¹ in the case of YCo(dmgh)₂, YNi(dmgh)₂ and YCu(dmgh)₂, respectively. The lowering of C=N stretching frequency suggests the coordination of nitrogen atoms and hence the encapsulation of dmgh₂ complexes. The νC=N band appears at 1611 cm⁻¹ for Me₂salen ligand. This band was reported to be shifted to 1600 cm⁻¹ in the case of simple complexes of Me₂salen [28]. No band that corresponds to the shifted νC=N could be seen in the spectra of encapsulated complexes due to the masking by broad zeolite band at the region 1650 cm⁻¹. However, the presence of aromatic bands in the spectra indicates the encapsulation of Me₂salen complexes.

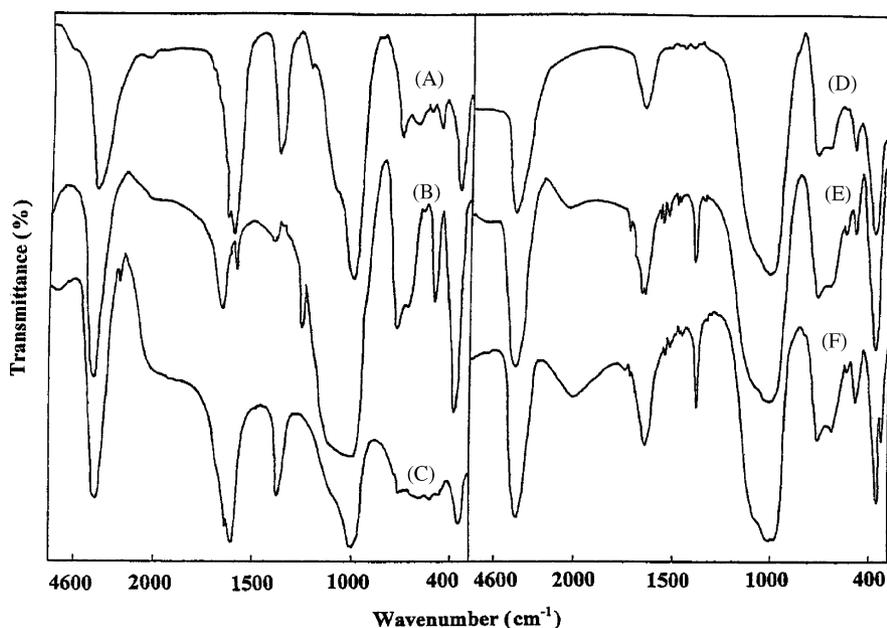


Fig. 3. FTIR spectra of encapsulated Co(II), Ni(II) and Cu(II) complexes of dmgH_2 (A–C) and Me_2salen (D–F).

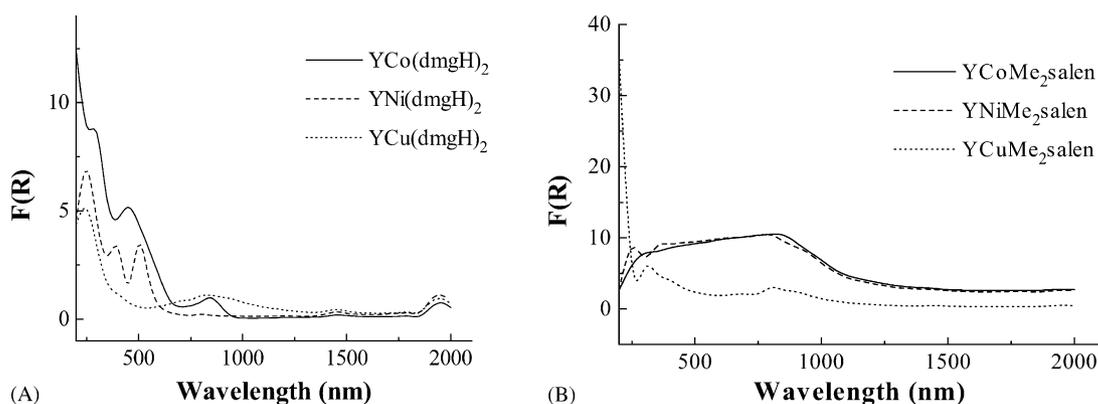


Fig. 4. UV-Vis spectra of encapsulated dmgH_2 (A) and Me_2salen (B) complexes.

3.5. Electronic spectroscopy

The UV-Vis electronic spectra of the encapsulated complexes are shown in Fig. 4. The positions of prominent absorption bands and magnetic moment values are given in Table 3. The geometries are tentatively assigned for the encapsulated complexes on the basis of adsorption bands and room temperature magnetic moment. The d–d transitions

Table 3
UV-Vis bands and magnetic moments

Sample	Absorptions, λ_{max} (nm)	Magnetic moment (BM)
$\text{YCo}(\text{dmgH}_2)_2$	840, 443, 268	5.25
$\text{YCoMe}_2\text{salen}$	750, 315	4.93
$\text{YNi}(\text{dmgH}_2)_2$	536, 387, 250	2.19
$\text{YNiMe}_2\text{salen}$	746, 374, 255	3.21
$\text{YCu}(\text{dmgH}_2)_2$	797, 242	1.86
$\text{YCuMe}_2\text{salen}$	801, 310	1.80

at 840 and 443 nm, and magnetic moment of 5.25 BM for $\text{YCo}(\text{dmgH}_2)_2$ are in agreement with the corresponding data reported for Co(II) complexes in octahedral symmetry [31]. $\text{YNi}(\text{dmgH}_2)_2$ shows an intense absorption at 536 nm, which is responsible for the reddish color of the sample and indicates square planar symmetry. However, the magnetic moment value of 2.19 BM suggests a slight distortion for the square planar geometry, which can lower the singlet–triplet energy separation and thus induces the partial paramagnetic nature [32]. In the case of encapsulated Co(II) and Ni(II) complexes of Me_2salen , the d–d bands are masked by the broad band in the UV region tailing to the visible region. However, magnetic moments of 4.93 BM for $\text{YCoMe}_2\text{salen}$ and 3.21 BM for $\text{YNiMe}_2\text{salen}$ indicate an octahedral symmetry [33]. It is well known that the electronic spectra of Cu(II) complexes give little information on their geometry. However, their magnetic moments of 1.83–1.86 BM imply square planar geometry [33], which could be further confirmed from the EPR data.

Table 4
EPR data of zeolite Cu(II) complexes

Sample	g_{\parallel}	g_{\perp}	g_{av}^a	$A_{\parallel} (\times 10^{-4} \text{ cm}^{-1})$	$A_{\perp} (\times 10^{-4} \text{ cm}^{-1})$	$g_{\parallel}/A_{\parallel}$
YCu(dmgh) ₂	2.32	2.04	2.13	158	29	147
YCuMe ₂ salen	2.31	2.01	2.11	139	47	166

$$^a g_{av} = (g_{\parallel} + 2g_{\perp})/3.$$

3.6. EPR spectroscopy

Table 4 depicts the X-band EPR spectra of encapsulated Cu(II) complexes recorded at 77 K. The spectra are typical of magnetically dilute Cu(II) ions, indicating that the copper complexes are finely dispersed within the diamagnetic zeolite matrix. In addition, the spectra are indicative of axial symmetry and exhibit hyperfine coupling originated from one copper nuclear spin of $I = \frac{3}{2}$ in the two g regions [34]. The EPR parameters observed for the encapsulated Cu(II) complexes are close to those reported for square planar Cu(II) ions surrounded by two N and two O atoms in YNa zeolite [35]. Extensive EPR studies of square planar Cu(II) complexes have shown that an increase in g_{\parallel} and decrease in A_{\parallel} can be due to the tetrahedral distortion of the square planar complex [36]. The $g_{\parallel}/A_{\parallel}$ ratio of 105–135 cm has been reported for Cu(II) ions in square planar symmetries. The higher $g_{\parallel}/A_{\parallel}$ ratios observed for YCu(dmgh)₂ and YCuMe₂salen could be attributed to the tetrahedral distortion of the square planar encapsulated complexes. However, in the case of zeolite complexes, the shift of $g_{\parallel}/A_{\parallel}$ ratio could also be possible due to either the axial coordination of zeolite oxygen atoms to the copper complex or an increase of the positive charge of the donor atoms due to their electrostatic interactions with Na⁺ ions in the lattice [37].

3.7. Catalytic activity

Decomposition of hydrogen peroxide was performed over zeolite-encapsulated complexes for the rapid screening of the samples for catalytic activity. The decomposition data are represented as a plot of volume of oxygen liberated

against time in Fig. 5. The decomposition rate is much higher for zeolite Cu(II) complexes, as compared to corresponding Co(II) and Ni(II) complexes. Furthermore, YCu(dmgh)₂ has shown faster decomposition rate than that of YCuMe₂salen. Transition metal complexes are known to effect the decomposition of hydrogen peroxide either by a free radical mechanism [38] or through the formation of active peroxy species in the coordination sphere [39]. While the electronic state of the metal site is important in the free radical mechanism, the latter is strongly influenced by the steric environment of the active sites. However, a reliable assessment of the structure and function of active sites has remained uncertain for many other reactions catalyzed by metal complexes. The decomposition behavior of the complexes is expected to provide valuable indications on the reactivity of active sites, which is mainly regulated by the electronic and steric factors.

The catalytic activity of zeolite complexes was evaluated for the oxidation of benzyl alcohol and ethylbenzene with hydrogen peroxide and oxygen. Hydrogen peroxide and oxygen are the preferred oxidants in zeolite systems, since they are highly mobile in the pores due to their smaller size. Furthermore, they are cheaper and sufficiently environment-friendly to be used on a commercial scale. However, aerobic oxidation is expected to occur at a slower rate due to the inability of molecular oxygen to be activated as compared to highly reactive species like peroxides. The catalytic nature of the oxidation was confirmed by running the reactions in the absence of any catalyst. Hydrogen peroxide alone is unable to oxidize the substrates to a significant extent, indicating that the reactions can occur only when a catalyst promotes them.

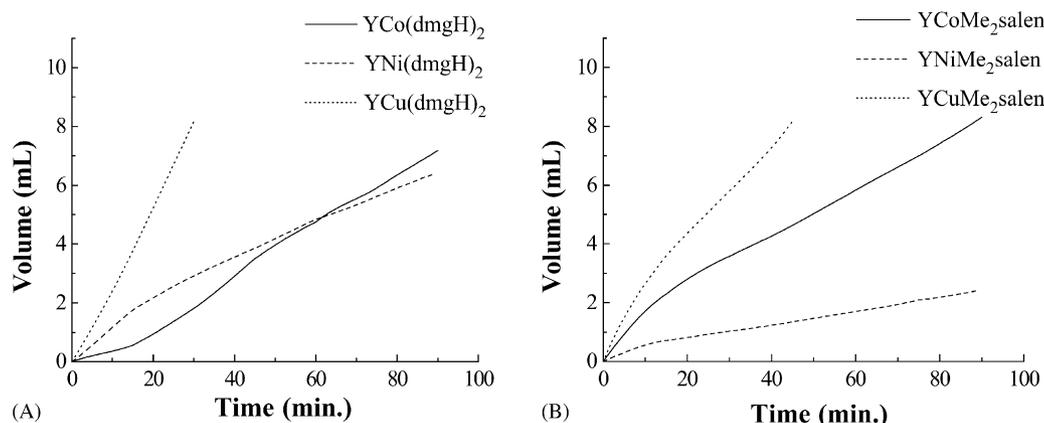


Fig. 5. Decomposition of hydrogen peroxide—oxygen liberated versus time plot of encapsulated dmgh₂ (A) and Me₂salen (B) complexes.

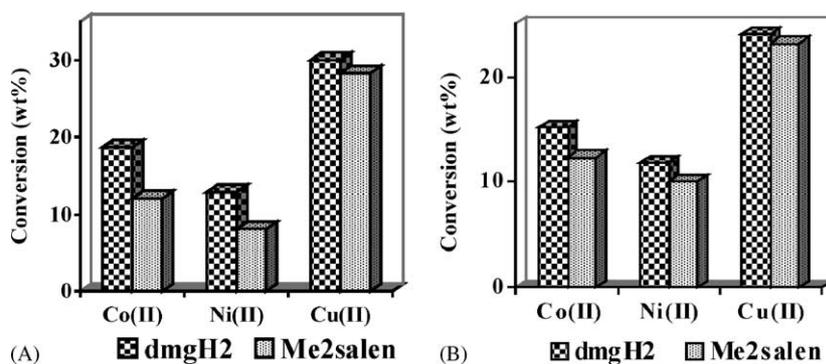


Fig. 6. Activities of zeolite complexes for the oxidation of benzyl alcohol (A) and ethylbenzene (B) with hydrogen peroxide at 323 K.

Since zeolite complexes are hybrid catalysts, it is important to run proper blank experiments to exactly find the role of host and guest molecules in catalysis. The oxidation reactions carried out over parent YNa zeolite have exhibited only negligible conversions, showing the inability of zeolite framework to catalyze the reactions. Leaching of metal complexes, if any, during the reaction can also cause serious errors in the activity of zeolite complexes. In representative tests, the catalyst was filtered out after the experiment and the progress of reaction in the solution phase was monitored for a long time. Lack of further reaction shows the absence of any catalytic active species in solution phase. The absence of complexes in solution was further confirmed by testing it for metal ions using atomic absorption spectrophotometry. The complexes are too intact in the pores to leach out and therefore, interference by free complexes in solution could be obviously rejected. In short, it could be concluded that

oxidation reactions occur due to the catalytic effect of encapsulated complexes and that neither zeolite host nor free complex has any major role in catalysis.

The catalytic activities of encapsulated Co(II), Ni(II) and Cu(II) complexes for the oxidation of benzyl alcohol and ethylbenzene with hydrogen peroxide at 323 K are represented in Fig. 6. Zeolite Cu(II) complexes have exhibited reasonably good activity, whereas Ni(II) and Co(II) complexes are weakly active. Zeolite Cu(II) complexes were thoroughly evaluated for catalytic efficiency at various conditions; the results are given in Table 5. Encapsulated Cu(II) complexes are found to be active for the aerobic oxidations in the presence of *t*-BuOOH as initiator. However, as expected, aerobic conditions are less effective as compared to the reactivity of hydrogen peroxide. In both cases, the activity increases on raising the reaction temperature from 323 to 343 K. It is interesting to note that the catalytic performances of zeolite

Table 5
Catalytic activities of zeolite Cu(II) complexes

Sample	Substrate	Oxidant	Temperature (K)	Percent conversion (wt.%)	TOF ^a		
YCu(dmgH) ₂	Benzyl alcohol	H ₂ O ₂	323	30.0	90		
			333	40.8	123		
			343	52.6	158		
	Ethylbenzene	H ₂ O ₂	323	24.0	72		
			333	33.6	101		
			343	46.3	139		
	Benzyl alcohol	O ₂	323	18.6	56		
			Ethylbenzene	O ₂	323	16.8	51
			Benzyl alcohol (poisoned)	H ₂ O ₂	323	14.2	43
YCuMe ₂ salen	Benzyl alcohol	H ₂ O ₂	323	28.3	84		
			333	36.8	109		
			343	47.7	141		
	Ethylbenzene	H ₂ O ₂	323	23.1	68		
			333	29.4	87		
			343	39.2	116		
	Benzyl alcohol	O ₂	323	16.8	50		
			Ethylbenzene	O ₂	323	11.1	33
			Benzyl alcohol (poisoned)	H ₂ O ₂	323	20.5	61

^a Measured in mmol of the substance reacted (mmol metal h)⁻¹.

Cu(II) complexes are comparable to the activity exhibited by the encapsulated salen complexes reported earlier [17,40]. Tetrahedrally distorted square planar geometries of zeolite Cu(II) complexes may account for their higher activity as the complexes readily provide the vacant coordination sites for oxygen binding. The octahedral symmetries of Co(II) and Ni(II) complexes might have rendered them weakly active.

Poison-tolerance of zeolite Cu(II) complexes was indirectly ascertained by evaluating their activity for the oxidation of benzyl alcohol in the presence of traces of pyridine which acts as a poison by coordinating irreversibly at the active site. The extent of deactivation of the catalyst, given by the loss in activity, could be related to the mobility of poison molecules at the active site. The activity results given in Table 5 show that YCu(dmgH)₂ has experienced a higher degree of deactivation (53% loss in activity), whereas YCuMe₂salen has exhibited better poison-tolerance (28% loss in activity). It is widely believed that the stereochemical environment of the active site has a profound influence on the mobility of molecules at the reaction center and hence on the poison-tolerance. Moderately higher activity of YCu(dmgH)₂ as compared to YCuMe₂salen could also be explained in terms of the enhanced mobility of reactants at the active sites.

The encapsulated complexes are believed to be stable and reusable due to the following reasons: (1) complexes are immobilized in the cavities, (2) reduced formation of inactive oxo and peroxo dimeric and other polymeric species in the cavities due to the steric effects of zeolite framework and (3) the interaction of encapsulated complexes with the zeolite lattice [14–21]. In order to ascertain the stability, the catalyst samples were filtered out after the reaction, washed with acetone and analyzed by IR spectra. No changes in spectra were observed, indicating that the coordination in encapsulated complexes is retained. Furthermore, the catalyst samples could be recovered from the reaction mixture and reused without any major loss in activity. The recycling ability also points out the absence of any irreversible deactivation of the encapsulated complexes, which is one of the major drawbacks of unsupported metal complexes in homogeneous catalytic reactions.

When metal oxide catalysts were used for the oxidation of benzyl alcohol in previous studies, small amounts of benzoic acid and benzyl benzoate were obtained as by-products [41]. The oxidation of benzyl alcohol with hydrogen peroxide over zeolite Cu(II) complexes gives benzaldehyde as the exclusive product. The formation of benzoic acid by the further oxidation of benzaldehyde or other side products could be effectively avoided by using encapsulated systems. Similarly, acetophenone was the only product formed by the oxidation of ethylbenzene over zeolite complexes. This shows that zeolite-encapsulated complexes can act as catalysts for the partial oxidation of organic compounds. Similar behavior for the partial oxidation of hydrocarbons has been found for zeolite-encapsulated iron-phthalocyanine

complexes [42]. Though zeolite complexes are mild oxidation catalysts, their unique selectivity for partial oxidation is particularly attractive for the design of environment-friendly catalysts.

4. Summary and conclusions

Y Zeolite-encapsulated Co(II), Ni(II) and Cu(II) complexes of the ligands have been synthesized using the flexible ligand method. Encapsulated complexes exhibit fairly clear evidence in the physico-chemical (SEM, XRD, surface area, pore volume) and IR spectral characterization for the well-defined inclusion and distribution of complexes in the zeolite matrix. Tentative assignments are made for the geometry of complexes on the basis of magnetic moment, UV-Vis and EPR data. Zeolite Cu(II) complexes are reasonably good catalysts for the partial oxidation of benzyl alcohol and ethylbenzene with hydrogen peroxide, whereas Co(II) and Ni(II) are weakly active. These catalysts are also active for oxidation at aerobic conditions. The catalytic behavior could be mainly attributed to the geometry of encapsulated complexes. Activity and poison-tolerance of the catalysts are dependent on the mobility of molecules, which is related to the diffusion limitations due to the steric hindrance at the metal center. Encapsulated complexes can be recovered and reused without the loss of catalytic activity. To summarize, zeolite-encapsulated complexes have interesting catalytic potential particularly with respect to the activity for partial oxidation and stability, and offer further scope to design efficient catalyst systems by an appropriate choice of guest and host materials.

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