Oxidation of phenol with H_2O_2 catalysed by Cu(II), Ni(II) and Zn(II) complexes of *N,N'*-bis-(salicylidene)diethylenetriamine (H_2saldien) encapsulated in Y-zeolite

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Abstract

Interaction of excess of *N,N'*-bis(salicylidene)diethylenetriamine (H_2saldien) with Cu(II), Ni(II) and Zn(II) exchanged zeolite-Y at ca. 90 °C leads to the encapsulation of ligand in the super cages of zeolite followed by complexation with metal ions. These encapsulated metal complexes have been characterised by IR and UV-Vis spectroscopic studies and thermal as well as X-ray diffraction (XRD) patterns. All encapsulated complexes serve as catalyst for the decomposition of H_2O_2 and for the oxidation of phenol to a mixture of catechol and hydroquinone using H_2O_2 as an oxidant. A suitable reaction condition has been optimised for [Zn(saldien)]-Y by considering the effect of various parameters such as different solvents, concentration of substrate, reaction time and amount of oxidant etc. for the maximum transformation of phenol. Thus, for a fixed amount of catalyst (0.025 g), 5.67 g of 30% H_2O_2 in 2 ml MeCN were sufficient enough to catalyse the oxidation of 4.70 g of phenol at 80 °C to give maximum transformation of phenol. Under the same reaction conditions the catalytic activity of these complexes follow the order: [Zn(saldien)]-Y (53%) > [Ni(saldien)]-Y (51%) > [Cu(saldien)]-Y (45%) after 24 h of reaction time. These catalytic activities were always found better over their respective non-encapsulated complexes.
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1. Introduction

Synthesis and catalytic activity of encapsulated metal phthalocyanate complexes in the cavity of Na-Y zeolite was first reported by Romanovsky and co-workers [1] in 1977 but further research in this area was considered only in the last decade. The study of the catalytic properties of transition metal complexes encapsulated in zeolite matrix is of great importance due to their industrial applications. Industrial pro-cesses utilising soluble transition metal complexes as catalyst face the problem of their recovery from the reaction product while the encapsulated complexes are easy to separate from the reaction product and share many advantageous features in common with homogeneous and heterogeneous catalysts. The reactant and the product selectivity due to the size constraints in the zeolite cages and the lifetime of the catalyst can also be increased by encapsulation. A molecule encapsulated in a zeolite cage is characterised by steric restriction, isolation from the other molecules by the zeolite lattice [2] and low mobility [3]. Besides, if the size of the molecule is comparable to the zeolite cage,

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the molecule may suffer a strong steric restriction in the cage. In such a case the molecule in the cage may show interesting properties, which are not seen under ordinary conditions. All these advantages promoted several research groups to investigate the catalytic properties of the complexes entrapped within the super cages of Y-zeolite. For example, selective oxidation/epoxidation of olefins [4–8], *p*-xylene [4,9,10] and styrene [10,11] oxidation of cyclohexanol [12] and phenol [4,10,13–15] and selective hydrogenation [16] have been reported using various transition metal complexes of *N,N′*-bis(salicylidene)ethane-1,2-diamine (H$_2$salen) and its derivatives encapsulated in zeolite. Catalytic activities of encapsulated complexes have also been reviewed [17]. We have recently reported the synthesis of [M(salpn)]-Y [where H$_2$salpn = *N,N′*-bis(salicylidene)propane-1,3-diamine, M = Fe(III), Cr(III), Bi(III), Ni(II), Cu(II) and Zn(II)] and studied their catalytic activity towards the oxidation of phenol [18,19].

In this paper we report the encapsulation of Cu(II), Ni(II) and Zn(II) complexes of *N,N′*-bis(salicylidene) diethylenetriamine (H$_2$saldien, **I**) by the flexible ligand method. These zeolite encapsulated metal complexes are screened as catalysts for the oxidation of phenol with the intention if selectivity in favour of catechol could be improved. The decomposition of H$_2$O$_2$ catalysed by these complexes has also been tested. For comparison purpose, we have also prepared respective neat complexes. Mn(III) complex of 5,5′-dinitrosaldien anion [*N,N′*-bis(5,5′-dinitrosalicylidene) diethylenetriamine (2−)] has only been prepared and used as catalyst for the epoxidation of (Z)-*β*-methylstyrene [20].
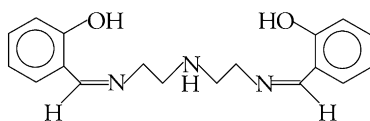
I (H$_2$saldien)

2. Experimental

2.1. Materials

Nitrates of Cu(II), Ni(II), and Zn(II), 30% aqueous H$_2$O$_2$ and phenol (Qualigens, India) were of Analar grade. Salicylaldehyde and diethylenetriamine (E. Merck, India) were used without further purification. Y-zeolite (Si/Al = 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were also of AR grade. Ligand H$_2$saldien was prepared as reported earlier [21].

2.2. Physical methods and analysis

The metal contents were measured by using Perkin-Elmer model 3100 Atomic Absorption Spectrophotometer. Thermogravimetric analyses of the pure as well as encapsulated complexes were carried out using TG Stanton Redcroft STA 780. X-ray diffractograms of solid catalysts were recorded using Philips PW 1140/90 X-ray powder diffractometer with Cu Kα target at our Institute's Instrumentation Centre. IR spectra were recorded as KBr pellet on a Perkin-Elmer model 1600 FT-IR spectrometer. Electronic spectra were recorded in Nujol on a Shimadzu 1601 UV-Vis spectrophotometer by layering mull of sample to inside of one of the cuvette while keeping another one layered with Nujol as reference. All catalysed reaction products were analysed using Nucon 5700 chromatograph fitted with FID detector and OV-17 (S.S.) column.

2.3. Preparations

2.3.1. Preparation of M-Y (metal exchanged zeolite-Y)

An amount of 5.0 g Na-Y zeolite was suspended in 300 ml distilled water containing metal nitrate (50 mmol) (nitrates of Cu(II), Ni(II) and Zn(II)). The mixture was then heated while stirring at 90 °C for 24 h. The solid was filtered, washed with hot distilled water till the filtrate was free from any metal ion content and dried for 12 h at 150 °C in air.

2.3.2. Preparation of [M(saldien)]-Y

An amount of 1.0 g M-Y and 2.5 g H$_2$saldien were mixed in a round bottom flask. The reaction mixture was heated at 100 °C for ca. 14 h in an oil bath with stirring, where ligand slowly diffused through the zeolite pores and formed complex with the metal ions. The resulting material was taken out and extracted with methanol till the complex was free from any unreacted H$_2$saldien. The uncomplexed metal ions present

in the zeolite were then removed by exchanging with aqueous 0.01 M NaCl solution. The resulting solid was finally washed with hot distilled water till no precipitation of AgCl on treating filtrate with AgNO$_3$. It was then dried at 150 °C for several hours to constant weight.

2.4. Catalytic activity studies

2.4.1. Decomposition of H$_2$O$_2$

An appropriate catalyst (0.025 g) was added to an aqueous solution of 30% H$_2$O$_2$ (5.5 g, 0.049 mol) at ambient temperature and the reaction mixture was kept stirring. After 1 or 2 h of stirring, the catalyst was filtered and the filtrate was diluted to 250 ml with distilled water. An aliquot of 10 ml of this solution was titrated against standard KMnO$_4$ solution after introducing 20 ml of 2 M H$_2$SO$_4$ and 20 ml of distilled water to it.

2.4.2. Oxidation of phenol

Catalytic experiments were carried out in a 50 ml glass reaction flask fitted with a water condenser. A general procedure was applied for all reactions except using varying amounts of reagents (i.e. catalyst, substrate, H$_2$O$_2$ and solvent) and changing time and temperature. In a typical reaction, phenol (4.7 g, 0.05 mol) and 30% aqueous H$_2$O$_2$ (5.67 g, 0.05 mol) were mixed in 2 ml of MeCN and the reaction mixture was heated in an oil bath with continuous stirring at 80 °C. An appropriate catalyst (0.025 g) was added to it and the reaction was considered to begin. The reaction products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot out.

3. Results and discussion

3.1. Syntheses and characterisation of catalysts

Synthesis of Cu(II), Ni(II) and Zn(II) complexes of H$_2$saldien encapsulated in the super cages of zeolite-Y was carried out by the flexible ligand method. This method consists of two steps: (i) the preparation of metal ion exchanged zeolite by exchanging Na$^+$ ions of Na-Y with 0.01 M solution of metal nitrates in aqueous solution and (ii) the heat-

ing of metal-exchanged zeolite in excess of ligand at 100 °C for ca.14 h. H$_2$saldien is able to diffuse easily through the zeolite pores due to its flexible nature and get complexed with a previously exchanged metal ion. The resulting complexes become too large to leach out of the cavities. The crude mass was subjected to Soxhlet extraction in methanol to remove excess ligand that remained uncomplexed in the cavities of the zeolite as well as located on the surface of the zeolite along with neat complexes formed, if any. The remaining uncomplexed metal ions in zeolite were removed by exchanging back with aqueous 0.01 M NaCl solution. The percent metal contents estimated by atomic absorption spectroscopy suggest the encapsulation of the metal complexes inside the super cages of the zeolite-Y.

The resulting catalysts were characterised by various physico-chemical techniques e.g. IR and electronic absorption spectroscopy and XRD as well as thermal analysis pattern. A comparison of the physico-chemical properties of these catalysts with that of the respective simple complexes, prepared by the reaction of H$_2$saldien with metal nitrates, was also carried out. The formulations of the encapsulated complexes are, thus, based on the respective simple complex and conclusion drawn from various studies (vide infra). The formula, colour and the percentage of metal content of various catalysts (i.e. encapsulated one) are presented in Table 1. Metal content of various metal-exchanged zeolite is also presented in Table 1 for comparison.

3.2. IR spectral studies

A partial list of IR spectral data is presented in Table 2. The intensity of the peaks in encapsulated

Table 1
Chemical composition, physical and analytical data of encapsulated catalysts

S. no.	Catalyst	Colour	Metal content (wt.%)
1	Cu-Y	Pale blue	7.60
2	Ni-Y	Greenish blue	6.82
3	Zn-Y	White	0.50
4	[Cu(saldien)]-Y	Pale green	0.34
5	[Ni(saldien)]-Y	Cream yellow	0.34
6	[Zn(saldien)]-Y	Off white	0.29

Table 2
IR spectral data (cm^{-1}) of ligand, pure and encapsulated complexes

Compound	ν(C=C), ν(C=N)	ν(M-O)/(M-N)
H$_2$saldien	1634, 1583	
[Cu(saldien)]-Y	1622, 1540	421, 470
[Cu(saldien)]	1623, 1540	414, 441, 465
[Ni(saldien)]-Y	1638, 1550	406, 431, 452, 466, 482
[Ni(saldien)]	1622, 1537	422, 467, 491
[Zn(saldien)]-Y	1642, 1535	411, 439, 455, 491
[Zn(saldien)]	1636, 1579	405, 463

complexes is, though, weak due to their low concentration in zeolite matrix, the spectra of encapsulated as well as their neat complexes showed essentially similar bands. Comparison of the spectra of these catalysts with the ligand provides evidence for the coordinating mode of ligand in catalysts. The ligand H$_2$saldien exhibits a broad band in the 2550–2700 cm^{-1} due to intramolecular hydrogen bonding between phenolic –OH and nitrogen of azomethine/secondary amine. Absence of this band in the spectra of encapsulated complexes indicates the destruction of the hydrogen bond followed by the coordination of phenolic oxygen after deprotonation. The sharp band appearing at 1583 cm^{-1} due to ν(C=N) (azomethine), shifts to lower wave number and appears at 1535–1579 cm^{-1}. This indicates the involvement of azomethine nitrogen

in coordination [22]. The appearance of two to five bands in the low frequency region (400–500 cm^{-1}) further indicates the coordination of nitrogen and oxygen to the metal. Unlike ν(C=N) stretching bands, the ν(C=C) stretching mode does not show any significant shift. The coordination of NH group could not be ascertained due to the appearance of broad band of water at ca. 3400 cm^{-1}. However, on the basis of literature report on [Ni(saldien)] [22], a non-involvement of the nitrogen of NH in coordination may also be concluded in all complexes. The existence of free –NH group in neat [Zn(saldien)] has been confirmed in solution by ^{1}H NMR spectral studies (vide infra). The IR spectral data, thus, support the encapsulation of the complexes in the super cages of the zeolite matrix.

3.3. ^{1}H NMR studies of ligand and neat [Zn(saldien)]

Comparison of ^{1}H NMR spectral data of the H$_2$saldien and the neat complex [Zn(saldien)] recorded in DMSO-d$_6$ further suppliments the conclusion drawn from IR data. The ^{1}H NMR spectrum of H$_2$saldien exhibits the following signals: 13.20 (s, 2H, OH), 8.50 (s, 2H, –CH=N–), 6.40–7.10 (m, 8H, aromatic) and 2.50–4.0 ppm (complex multiplet, ~8H, CH$_2$). The signal due to –NH proton could not be located probably due to its involvement in

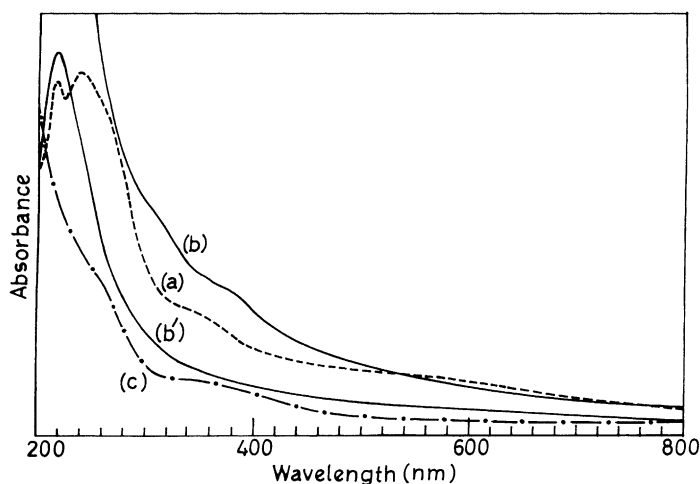Fig. 1. Electronic spectra of (a) [Cu(saldien)]-Y, (b) [Ni(saldien)]-Y with concentrated paste with Nujol, (b′) [Ni(saldien)]-Y with dilute paste with Nujol and (c) [Zn(saldien)]-Y.

hydrogen bonding. The disappearance of phenolic signal and down field shift (8.59 ppm) of azomethine signal indicates the coordination of phenolic oxygen after deportation and azomethine nitrogen atoms. The appearance of –NH proton at 12.67 ppm clearly indicated the non-involvement of NH group in coordination. Other signals i.e. signals due to aromatic and CH_2 protons appear nearly at the same position. ^{1}H NMR spectrum of [Ni(saldien)] could not be recorded due to its partial paramagnetic nature of complex as noticed earlier [22].

3.4. Electronic spectral studies

The electronic spectra of the ligand, neat as well as encapsulated complexes are presented in Table 3. Fig. 1 represents the electronic spectra of encapsulated complexes. The electronic spectrum of the H_2saldien exhibits four bands at 402, 316, 255 and 220 nm. As molar absorptivity of the first two bands are comparatively low, these bands seem to be a splitted band of n–π^* transition. The other two bands are assigned as π–π^* and ϕ–ϕ^* transitions, respectively. The appearance of a weak shoulder at 280 nm is indicative of the presence of intra molecular hydrogen bonding in ligand. This band is completely absent in all complexes thereby indicating the destruction of hydrogen bonding and coordination of phenolic oxygen to metal ion. The spectrum of [Cu(saldiene)]-Y in Nujol displays two bands at 341 and 573 nm in the visible region. The former band is probably due to symmetry forbidden ligand to metal charge transfer transition similar to that observed in [Cu(CH$_3$COO)$_2$(H$_2$O)] at 370 nm [23], while latter one is due to d–d transition of the complex. These data also compare closely

with [Cu(salpn)]-Y, where square planar structure has been suggested [19]. A square planar structure seems to be more appropriate as an unusually long Cu–N (of NH) bond length has been observed in related neat complex [Cu(saldipa)] (H_2saldipa = N,N'-bis(salicylidene-γ-iminopropyl)amine) where ligand has even better flexibility [24]. Other two bands appearing at 215 and 247 nm can be assigned as π–π^* and ϕ–ϕ^* transitions, respectively. The absorption spectrum of [Ni(saldien)]-Y exhibits two bands at 372 and 296 nm which is similar to that reported by Coleman et al. for pseudo square planar complex [Ni(saldien)] [22]. Other band appearing at 218 nm is due to the intra-ligand band ϕ–ϕ^*. As expected zinc complex exhibits only intra ligand bands. On the basis of spectral evidences the square planar structure **II** for the catalysts encapsulated in the zeolite-Y has been suggested.
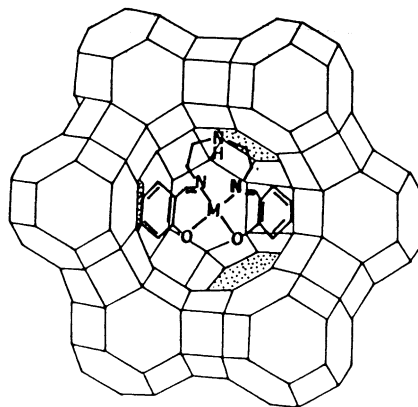
II (proposed structure of [M(saldien)]-Y (M = Cu(II), Ni(II) and Zn(II)); structure of zeolite frame work has been adopted from [25]).

3.5. Thermogravimetric studies

The thermogravimetric analysis data along with the percent weight loss at different steps and their assignments are presented in Table 4. TGA and DTA profile of one representative complex [Cu(saldien)]-Y is reproduced in Fig. 2. The decomposition of all complexes occurs in two major steps. An endothermic loss of intra-zeolite water occurs between temperature 150 and 270 °C in [Cu(saldien)]-Y and [Ni(saldien)]-Y and between 150 and 190 °C in [Zn(saldien)]-Y. The

Table 3
Electronic spectral data of ligand and complexes

Compound	Solvent	λ_{max} (nm)
H_2saldien	Methanol	402, 316, 280, 255, 220
[Cu(saldien)]-Y	Nujol	572, 341, 246, 215
[Cu(saldien)]	DMF	588, 369, 269
[Ni(saldien)]-Y	Nujol	371, 297, 211
[Ni(saldien)]	DMF	393, 333, 267
[Zn(saldien)]-Y	Nujol	368, 252, 206
[Zn(saldien)]	DMF	398, 318, 268

Table 4
Thermogravimetric analysis data of catalysts

Catalyst	Temperature range (°C)	Weight loss (%)	Group lost[a]	Type of loss
[Cu(saldien)]-Y	150–270	22.0	nH$_2$O	Endothermic
	270–600	6.0	L	Exothermic
[Ni(saldien)]-Y	150–240	18.0	nH$_2$O	Endothermic
	240–740	9.0	L	Exothermic
[Zn(saldien)]-Y	150–190	16.0	nH$_2$O	Endothermic
	190–655	9.0	L	Exothermic

[a] L stands for saldien^{2-}.

presence of at least four or more intra-zeolite water molecules has earlier been observed in [Cu(salen)]-Y [12]. In these complexes we expect the presence of even more intra-zeolite water as these catalysts were dried only at 150 °C. The second step involves the slow but exothermic weight loss in a wider temperature range due to decomposition of the chelating ligand. A very small percent weight loss (about 9% in Ni(II) and Zn(II) complexes and 6% in Cu(II) complex) indicates the presence of only small amount of

metal complexes in the cavities of the zeolite. This is in agreement with the low percent metal content estimated by atomic absorption (vide supra).

3.6. X-ray powder diffraction study

The X-ray powder diffraction (XRD) patterns of Na-Y, metal exchanged zeolite and encapsulated metal complexes along with simple complexes were recorded at 2θ values between 5 and 70° to study the crystallinity and to ensure encapsulation. The XRD patterns of metal exchanged zeolite and their respective encapsulated complexes are essentially similar to that of Na-Y, though slight change in the intensity of the bands has been noticed. These observations indicate that the framework of the zeolite has not undergone any significant structural changes during incorporation of the catalysts i.e. crystallinity of zeolite-Y is preserved during encapsulation. The representative XRD patterns of Cu-Y and [Cu(saldien)]-Y are reproduced in Fig. 3. A new band with a 2θ value of 25.1° was located in Ni-Y, [Ni(saldien)]-Y and [Ni(saldien)] while another band
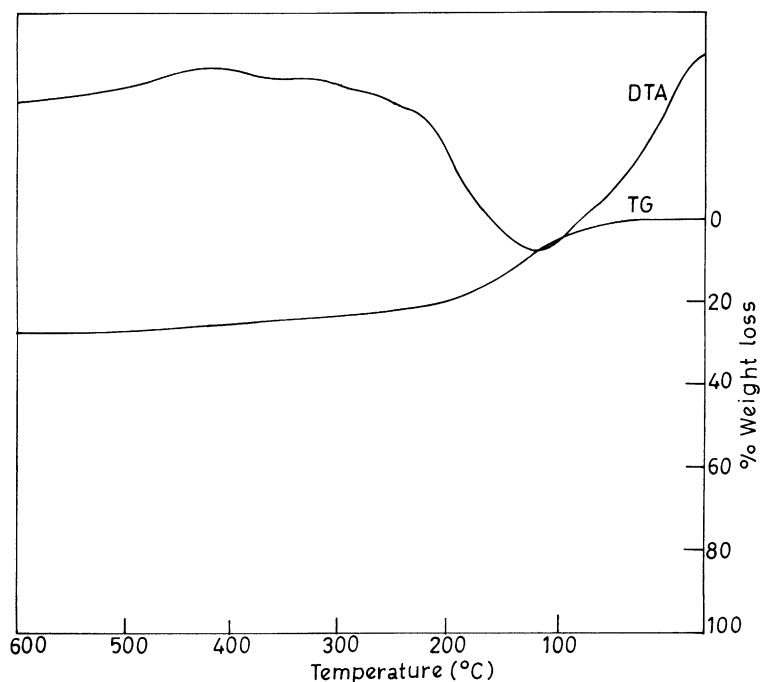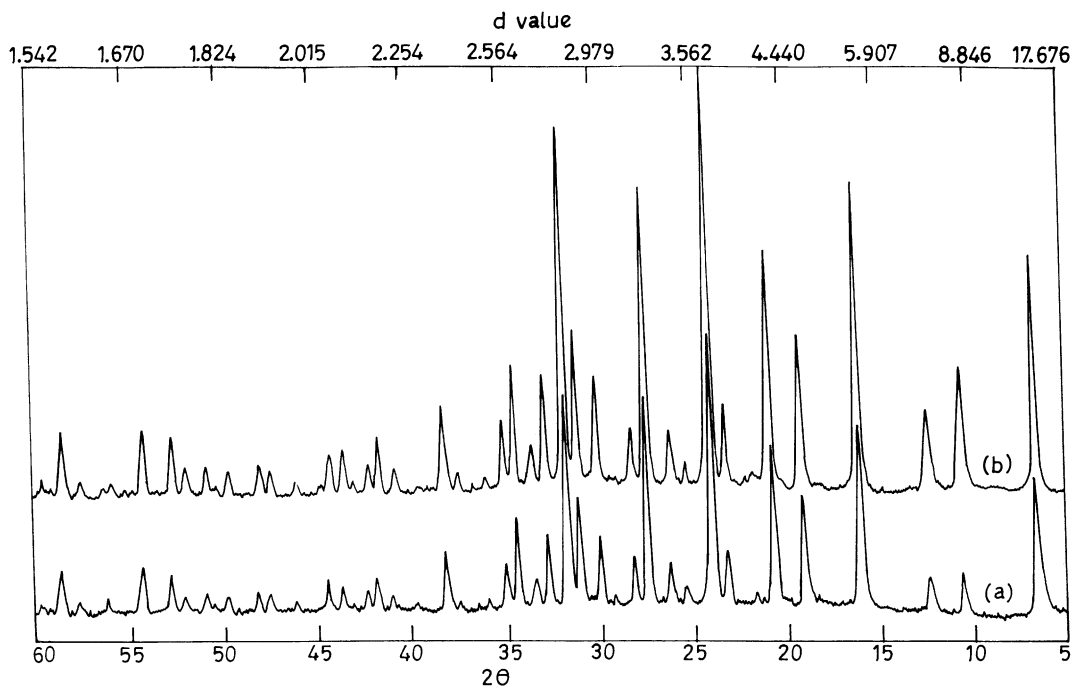

Fig. 2. TGA and DTA profile of [Cu(saldien)]-Y.

Fig. 3. XRD pattern of Cu-Y (a) and [Cu(saldien)]-Y (b).

with a 2θ value of $16.8°$ could be located only in Ni-Y and [Ni(saldien)]-Y. Similarly XRD patterns of Cu-Y and [Cu(saldien)]-Y exhibited two new bands with a 2θ value of 25.6 and $46.2°$ while Zn-Y and [Zn(saldien)]-Y showed only one new band with a 2θ value of $17.8°$. These clearly suggest the presence of metal complexes in zeolite matrix.

3.7. Decomposition of H_2O_2

The catalytic activity of all three encapsulated catalysts were tested for the decomposition of H_2O_2 at two different contact times (1 and 2 h) and the relevant data are presented in Table 5. It is clear from the data that the decomposition of H_2O_2 using all catalysts is rather slow (2.7–3.0%) within 1 h of contact time. The turn over frequency (TOF) calculated is also nearly same (about 25). On increasing the contact time to 2 h, all catalysts performed better and follow the order of decomposition: Ni(II) (14.9%) > Zn(II) (9.9%) > Cu(II) (9.6%). These results thus indicate that all catalysts require a relatively longer contact time to improve decomposition of H_2O_2, which in turn would be helpful in improving the oxidation reactions using this as an oxidant.

3.8. Oxidation of phenol

As hydroxyl group of phenol is ortho and para directing, the oxidation of phenol is expected to give two products viz. catechol and hydroquinone as shown by Eq. (1). The presence of these two products were also observed with a mass balance of about 96% when phenol was catalysed by Cu(II), Ni(II) and Zn(II) complexes of H_2saldien encapsulated in the cavity of zeolite-Y using H_2O_2 as an oxidant. Minor product (e.g. polymeric materials), if any, is not detectable in GC under the condition used herein. For comparison, the respective neat complexes viz. [Cu(saldien)], [Ni(saldien)] and [Zn(saldien)] were also examined for their catalytic performance.
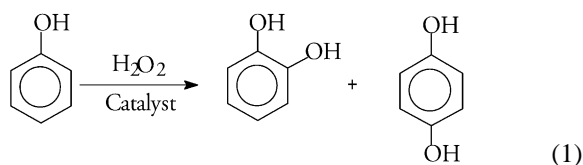
$$\text{phenol} \xrightarrow[\text{Catalyst}]{H_2O_2} \text{catechol} + \text{hydroquinone} \qquad (1)$$

Table 5
Percentage decomposition of H_2O_2 after 1 and 2 h of contact time

Catalyst	Percentage of H_2O_2 reacted after 1 h	TOF	Percentage of H_2O_2 reacted after 2 h	TOF
[Cu(saldien)]-Y	2.7	25.0	9.6	31.8
[Ni(saldien)]-Y	2.7	24.6	14.9	47.8
[Zn(saldien)]-Y	3.0	26.9	9.9	39.8

TOF: turn over frequency—moles of substrate converted per mole of metal (in solid catalyst) per hour.

In order to achieve suitable reaction conditions for maximum transformation of phenol as well as better selectivity for the formation of catechol the following parameters were studied in detail using [Zn(saldien)]-Y as a representative catalyst:

- Effect of H_2O_2 concentration (moles of H_2O_2 per mole of phenol) and other oxidants.
- Effect of phenol concentration (moles of phenol per mole of H_2O_2).
- Effect of amount of catalyst.
- Effect of temperature.
- Effect of type and volume of solvent (keeping other parameters fixed).

3.8.1. Effect of H_2O_2 concentration and other oxidants

The effect of H_2O_2 concentration on the phenol oxidation reaction is illustrated in Fig. 4. Three different molar ratios of H_2O_2 to phenol were used (1:1, 2:1, 0.5:1 mol) in which the amount of phenol was kept
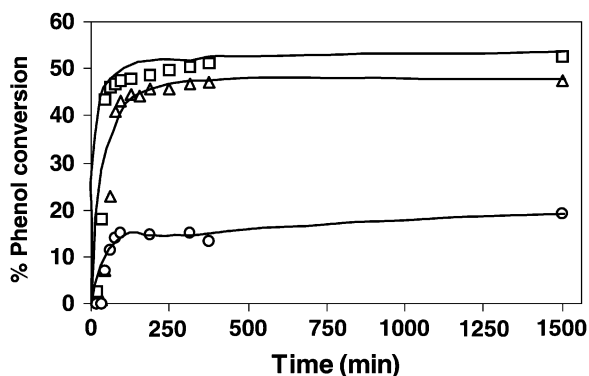

Fig. 4. Effect of H_2O_2 concentration on phenol oxidation: (○) 0.5:1, (□) 1:1 and (△) 2:1 moles (H_2O_2/phenol) for a fixed amount of 0.05 mole of phenol.

fixed at 4.7 g (0.05 mol) in 2 ml of MeCN. It is clear from the figure that the conversion of phenol is considerably faster in the first 1 h of reaction in all the cases. However, at the expense of time further conversion is rather slow. The percentage phenol conversion also increases with the increment of H_2O_2 to phenol ratio. This conversion is substantial from 0.5:1 to 1:1 (H_2O_2/phenol) ratio. Whereas it is just marginal for higher ratio i.e. beyond 1:1 (H_2O_2/phenol) molar ratio and then goes down with the concentration of 2:1 (H_2O_2/phenol) molar ratio. The reason for this may be due to the dilution of the reaction mixture by the presence of larger amount of water molecules in H_2O_2 solution. Further, for 1:1 molar ratio, the addition of oxidant in three equal batches at every 1 h interval even does not improve the transformation of phenol. The maximum transformation of ∼51% in first 6 h and ∼53% after 24 h has been obtained in both cases. This result clarifies that large H_2O_2 concentration or batch addition is not an essential condition to maximise phenol transformation.

Using NaOCl (∼6% in H_2O) or tert-butylhydroperoxide (70% in H_2O) as oxidant did not show appreciable oxidation (ca. 2%) of phenol under similar conditions as mentioned above.

3.8.2. Effect of phenol concentration

While keeping parameters such as amount of catalyst (0.025 mg), volume and type of solvent (2 ml MeCN) and amount of oxidant (5.67 g) fixed, the catalytic reaction was performed using three different molar ratios of phenol to H_2O_2 viz. 0.33:1, 1:1 and 2:1 at 80 °C. Among these ratios, as shown in Fig. 5, maximum conversion was observed again with 1:1 molar ratio only. The rate of increment of percentage of phenol conversion is also fastest with these molar ratio concentrations. Increasing or decreasing the concentration of phenol beyond this molar ratio under the same reaction conditions led to lower conversions.

3.8.3. Effect of amount of catalyst

The effect of amount of catalyst on the rate of reaction is illustrated in Fig. 6. Among three different amounts (e.g. 0.01, 0.025 and 0.1 g) of catalyst an amount of 0.025 or 0.1 g gave almost comparable results for the fixed amount of oxidant and substrate in 2 ml of MeCN (as mentioned in Section 3.8.2). Lower the amount of catalyst to 0.01 g resulted in the
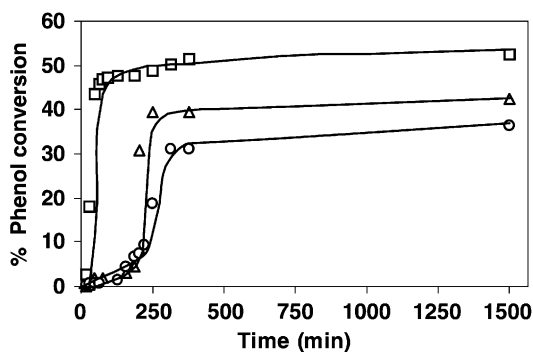
Fig. 5. Effect of phenol: H_2O_2 molar ratio on phenol oxidation (○) 0.33:1, (□) 1:1 and (△) 2:1.

transformation of ca. 30% phenol in 6 h of reaction time. Such phenomenon has previously been observed by others and us and has been interpreted in terms of thermodynamic and mass transfer limitations at high reaction rate etc. [18,19,26] We expect these factors applicable here also. Thus, 0.025 g of catalyst is sufficient enough to give its best performance.

3.8.4. Effect of temperature

Temperature of the reaction also has influence on the performance of the catalyst for phenol conversion. Three different temperatures (50, 65 and 80 °C) were used while keeping other parameters fixed (i.e. 0.025 g [Zn(saldien)]-Y, 5.67 g H_2O_2 and 4.7 g phenol) for the catalytic tests in 2 ml of MeCN. The activity of the catalyst was found to increase as the temperature was

Fig. 6. Effect of catalyst weight on phenol oxidation: (□) 0.01, (●) 0.025 and (△) 0.1 g.

raised from 50 to 80 °C. It is observed that the time required to achieve the maximum (steady state) conversion (∼47%) is around 1.5 h at 80 °C, whereas, the same was achieved at 3 and 4 h, respectively, at 65 and 50 °C. Thus, it is clear that 80 °C is the minimum required temperature to supply sufficient energy to reach the energy barrier of phenol transformation.

3.8.5. Effect of type and volume of solvents

Solvents have great influence on the reaction rates through competitive sorption/adsorption phenomenon in the super cages of zeolite. Polarity, hydrophilicity and size of the solvent molecule may also play some role on the reaction rate. In the present study, five different solvents viz. MeCN, ethyl acetate (EA), hexane, ethanol (EtOH) and 1,2-dichloroethane (1,2-DCE) were used to see their effect on the reaction rate. Fig. 7 shows the percentage phenol conversion as a function of time for all these solvents. Although it is difficult to explain here as to which property of the solvent has influenced the phenol conversion most, it is clear from the plot that acetonitrile is the best solvent among all. The maximum percent phenol conversion obtained with various solvents is in the order, MeCN (53%) > EA (44%) > hexane (41%) > ethanol (25%) > 1,2-DCE (9%). However, within the solvent system, 2 ml of MeCN was found to be sufficient enough to perform the reaction to give best result. Increasing the amount of solvent and with no added solvent, the catalytic reaction always led to the poor performance. A decreased solvent amount (1 ml) was found not sufficient to dissolve the substrate and formed a non-homogeneous reaction mixture.
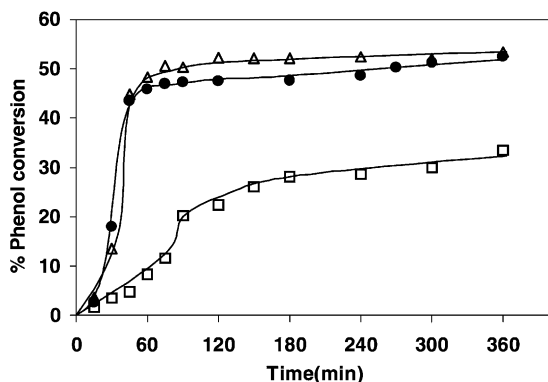
3.9. Catalytic activity of [Cu(saldien)]-Y and [Ni(saldien)]-Y

After acquiring the best suitable reaction conditions for [Zn(saldien)]-Y, the oxidation of phenol was also studied using [Cu(saldien)]-Y and [Ni(saldien)]-Y as catalyst under same reaction conditions. It was observed that using 0.025 g of catalyst, [Ni(saldien)]-Y showed comparable catalytic activity to that of [Zn(saldien)]-Y with 51% conversion of phenol, which was followed by [Cu(saldien)]-Y with 45% conversion after 24 h of reaction time. These observations indicate that all the three catalysts have potential catalytic activity for the oxidation of phenol.
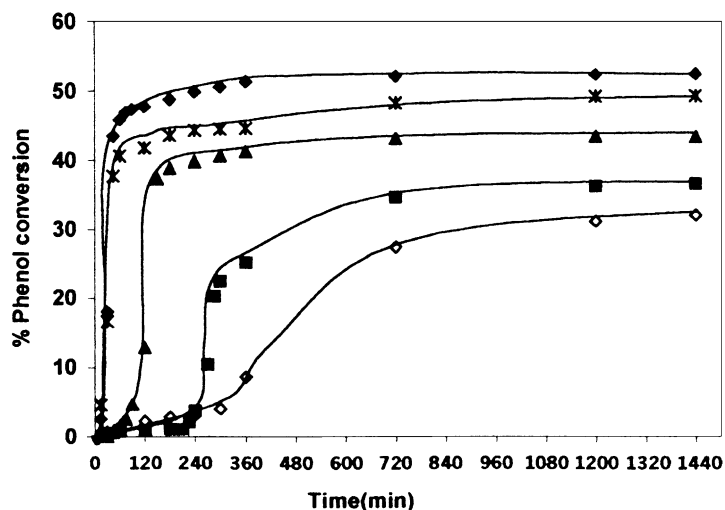
Fig. 7. Effect of various solvents on oxidation: (◆) MeCN, (■) EtOH, (▲) hexane, (◇), 1,2-dichloroethane and (✗) ethylacetate.

3.10. Catalytic activities comparison of neat and encapsulated complexes

Catalytic oxidation of phenol using the corresponding neat complexes viz. [Cu(saldien)], [Ni(saldien)] and [Zn(saldien)] as catalyst and H_2O_2 as oxidant in 2 ml MeCN have also been studied. Interestingly, neat complexes have also shown good activity, though, conversion is lower as expected. Among these catalyst [Zn(saldien)] shows maximum conversion of 37.4% after 6 h of reaction time, while activities of [Ni(saldien)] and [Cu(saldien)] are comparable with a conversion of about 29%. Table 6 presents all these data along with percent selectivity for the formation

Table 6
Percent selectivity of catechol and hydroquinone formation and percent conversion of phenol after 6 h of reaction time

Compound	Conversion of phenol (%)	Selectivity (%)	
		Catechol	Hydroquinone
[Cu(saldien)]-Y	46.0	68.3	31.7
[Cu(saldien)]	29.3	75.5	24.5
[Ni(saldien)]-Y	50.2	68.1	31.9
[Ni(saldien)]	29.6	62.5	37.5
[Zn(saldien)]-Y	51.3	67.4	32.6
[Zn(saldien)]	37.4	70.0	30.0

of catechol and hydroquinone. It is clear from the table that neat complexes are more selective for the catechol formation over encapsulated ones, except the [Ni(saldien)] which shows fewer selectivity (62.5%) than [Ni(saldien)]-Y (68.1%). On increasing the reaction time from 6 to 24 h, only minor increase in the transformation of phenol as well as percent selectivity for the formation of catechol and hydroquinone were observed for both types of catalysts.

3.11. Oxidation of 2,4-dichlorophenol and 1-naphthol

Under the reaction conditions optimised for the oxidation of phenol, the oxidation of 2,4-dichlorophenol was also carried out using [Zn(saldien)]-Y as catalyst. The result shows that only about 3% oxidation of 2,4-dichlorophenol was observed, which is much less in comparison to the phenol oxidation. Such less conversion is expected as we go from smaller to bulkier substituents, their entrance through the opening of the zeolite pore becomes more and more difficult which would ultimately result in lower catalytic activity. However, oxidation of 1-naphthol was found better (∼7%), though it is bulkier than 2,4-chlorophenol. The presence of two deactivating groups (i.e. dichloro substituents) is probably responsible for lower conversion.

4. Conclusions

Cu(II), Ni(II) and Zn(II) complexes of H_2saldien have been encapsulated in the super cages (α-cages) of zeolite-Y. Spectroscopic studies, XRD pattern and
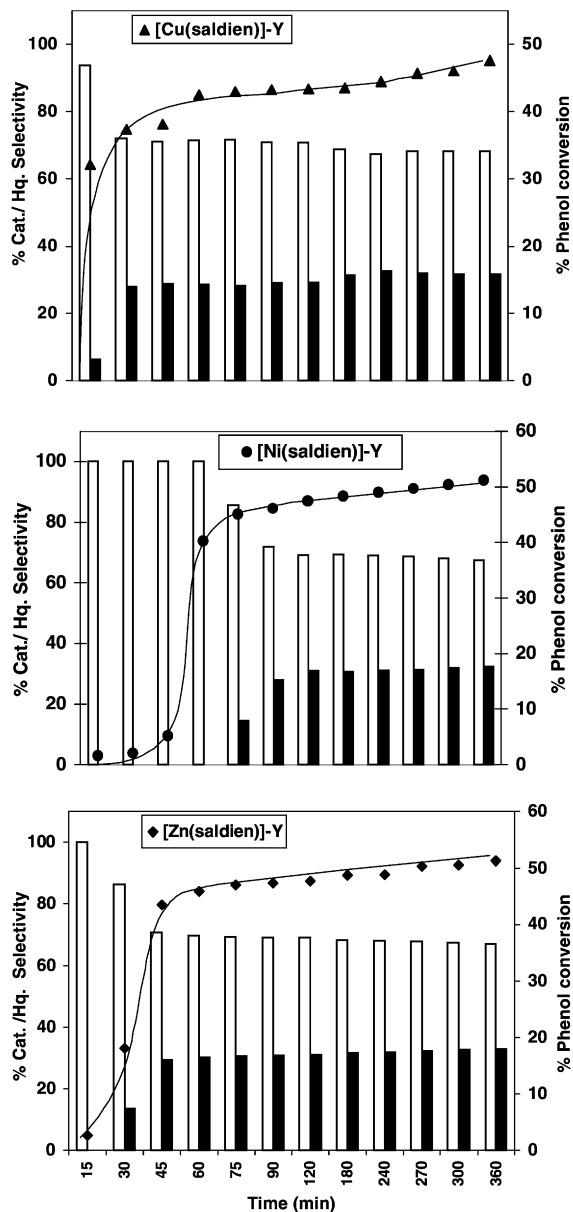

Fig. 8. Bar diagram showing selectivity of catechol and hydroquinone formation and plot showing percentage phenol conversion as a function of time using [Cu(saldien)]-Y (top), [Ni(saldien)]-Y (middle) and [Zn(saldien)]-Y [bottom] as catalyst.

thermal as well as chemical analyses present a clear evidence for their encapsulation. This was further supported by the fact that no leaching of metal ions was detected in the solution when a blank reaction was carried out by considering 5.5 g H_2O_2, 0.025 g catalyst in 2 ml of MeCN at 80 °C. Several factors such as amount of oxidant, catalyst, volume and type of solvents and temperature of the reaction mixture affect on the performance of these catalysts. The steric hindrance or size of the substrates has direct influence on the performance of these catalysts. These encapsulated complexes are mild catalysts for the decomposition of H_2O_2 while good catalysts for the oxidation of phenol to a mixture of catechol and hydroquinone with good catechol selectivity. Fig. 8 summarises percent phenol conversion and selectivity of both the products at various reaction time using [Zn(saldien)]-Y as catalyst. Neat complexes are also good catalysts but result in considerably less conversion of phenol in comparison to encapsulated one. The percent selectivity for the formation of catechol is always higher for both types of catalysts than hydroquinone. Comparable IR spectral patterns of fresh and used encapsulated catalysts suggest that these can be used further for catalytic study.

Acknowledgements

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