

Oxidation of phenol, styrene and methyl phenyl sulfide with H₂O₂ catalysed by dioxovanadium(V) and copper(II) complexes of 2-aminomethylbenzimidazole-based ligand encapsulated in zeolite-Y

Mannar R. Maurya^{a,*}, Anil K. Chandrakar^b, Shri Chand^b

^a Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India

^b Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247 667, India

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Abstract

Interaction of oxovanadium(IV) exchanged zeolite-Y with the Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole (Hsal-ambmz) in refluxing methanol followed by aerial oxidation leads to the formation of encapsulated dioxovanadium(V) complex, [VO₂(sal-ambmz)]-Y(**1**). Similar reaction with copper(II) exchanged zeolite-Y followed by its treatment with aqueous NaCl gave encapsulated copper(II) complex, [Cu(sal-ambmz)Cl]-Y(**2**). These encapsulated complexes have been characterized by spectroscopic studies, thermal analysis and scanning electron micrographs (SEMs) as well as X-ray diffraction patterns. 3D model structure generated for neat complex [VO₂(sal-ambmz)] suggests that zeolite-Y can accommodate these complexes in its nano-cavity without any strain. The encapsulated materials are active catalysts for the oxidation of phenol, styrene and methyl phenyl sulfide using H₂O₂ as an oxidant. Under the optimised reaction conditions about 42% conversion of phenol was obtained with these catalysts where the selectivity of catechol varied in the order: **2** (73.9%) > **1** (65.2%). With the conversion of 97.0% with **1** or 56.7% with **2**, the oxidation of styrene gave styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde as major products. A maximum of 96.1% (with **1**) conversion of methyl phenyl sulfide was observed in which the selectivity of major product methyl phenyl sulfoxide was found to be ca. 98%.

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1. Introduction

Heterogeneous catalysts have played a key role in the development of industrial processes for chemical industry. There are three general methods to heterogenise homogeneous catalysts: (i) by polymerization of homogeneous catalyst itself [1–5] and thus making them insoluble in solvents, (ii) by immobilization of homogeneous catalyst through covalent bonding with polymeric materials [6–9] or materials like functionalized MCM-41, SBA-15, etc. [10,11] and (iii) by encapsulating them in the nano-cavity of, e.g. zeolites [12–16]. Latter two methods provide additional characteristic properties such as activity, selectivity, thermal stability and reusability of the catalysts. In recent years

zeolite encapsulated metal complexes (ZEMC) have provided the opportunity to develop catalytic process for the selective oxidation, alkylation, dehydrogenation, cyclization, amination, acylation, isomerisation and rearrangement of various substrates and are able to produce intermediates as well as most industrial products [12–15].

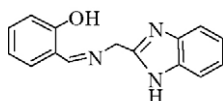
Liquid phase hydroxylation of phenol, by molecular oxygen and H₂O₂, is industrially important reaction. Several heterogeneous catalytic methods have been developed for the oxidation of phenol and wide range of products selectivity has been reported [17–21]. The catalysts based on zeolite encapsulated metal complexes have played excellent role in this regard [22–24]. We have reported oxidation of phenol using salen (H₂salen = *N,N'*-bis(salicylidene)-1,2-diaminoethane) based transition metal complexes and have shown that selectivity towards the formation of catechol was ca. 90% with [VO(salen)] encapsulated in zeolite-Y [25].

* Corresponding author. Tel.: +91 1332 285327; fax: +91 1332 273560.
E-mail address: rkmanfcy@iitr.ernet.in (M.R. Maurya).

Styrene epoxide, an important intermediate for the manufacture of perfumery chemical phenylethyl alcohol, is oxidation product of styrene. Homogeneous and heterogeneous catalysts have been used for the epoxidation of styrene [26–31].

In this work, we have encapsulated copper(II) and dioxovanadium(V) complexes of Schiff bases derived from salicylaldehyde and 2-aminomethylbenzimidazole (Hsal-ambmz, **I**) in the super cages of zeolite-Y and characterized. Their catalytic activities have been tested for the liquid phase oxidation of phenol and styrene.

Enzyme vanadate-dependent haloperoxidases catalyse the oxidation of sulfides (thioethers) to sulfoxides and further to sulfones [32]. Vanadium complexes are known to mimic sulfoxidases activity [31,33,34]. We have, therefore, tested sulfoxidases activity also with encapsulated vanadium complex in question.



I: Hsal-ambmz

2. Experimental

2.1. Materials

Analytical reagent grade cupric nitrate, cupric chloride, 30% aqueous H_2O_2 , salicylaldehyde (sal), *o*-phenylenediamine were obtained from E. Merck, India. Vanadyl sulfate penta hydrate, glycine and phenol were obtained from Loba Chemie, India. Methyl phenyl sulfide obtained from Alfa Aesar, U.S.A. and styrene from Acros Organics, New Jersey, U.S.A. were used as such. Zeolite-Y (Si/Al = ca. 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were of AR grade. 2-Aminomethylbenzimidazole dihydrochloride (ambmz·2HCl) was prepared following the procedure reported in the literature [35].

2.2. Physical methods and analysis

Copper and vanadium were analysed using inductively coupled plasma (ICP; Labtam 8440 plasmalab) after leaching the metal ions with conc. nitric acid and diluting with distilled water (for copper) or with very dilute aqueous KOH solution (for vanadium) to specific volume in volumetric flask. Electronic spectra were recorded in Nujol using Shimadzu 1601 UV–vis spectrophotometer by layering the mull of the sample to inside of one of the cuvettes while keeping the other one layered with Nujol as reference. Spectra of neat complexes were recorded in methanol. IR spectra were recorded as KBr pellet on a Nicolet NEXUS Avigent 1100 series FT-IR spectrometer after grinding the sample with KBr. Thermogravimetric analyses of pure as well as encapsulated complexes were carried out using TG Stanton Redcroft STA 780. X-ray powder diffractograms of solid catalysts were recorded using a Bruker AXS D8 Advance X-ray powder diffractometer with a Cu $K\alpha$ target. All catalysed reaction products were analysed using thermoelectron gas-chromatograph having HP-1 capillary column (30 m \times 0.25 mm \times 0.25 μ m) and FID

detector. Scanning electron micrographs (SEMs) of catalysts were recorded on a Leo instrument model 435VP. The samples were dusted on alumina and coated with thin film of gold to prevent surface changing and to protect the surface material from thermal damage by electron beam. In all analysis, a uniform thickness of about 0.1 mm was maintained.

2.3. Preparations

2.3.1. Preparation of Hsal-ambmz

Ligand Hsal-ambmz was prepared as reported previously [31]. An aqueous solution of ambmz·2HCl (1.10 g, 5 mmol in 15 ml) was neutralized by adding aqueous K_2CO_3 solution (0.83 g, 6 mmol). A methanolic solution of salicylaldehyde (0.61 g, 5 mmol in 10 ml) was added drop-wise to the above solution with stirring within 1 h. During this period, yellow solid slowly separated out which was filtered, washed thoroughly with water followed by petroleum ether and dried in vacuo at room temperature. Finally, it was recrystallised from minimum amount of acetonitrile. Yield 70%. Anal. found: C, 71.32%; H, 5.37%; N, 16.52%. Calcd. for $C_{15}H_{13}N_3O$ (251.29): C, 71.70%; H, 5.21%; N, 16.72%. 1H NMR (DMSO- d_6 , δ /ppm): 12.90 (b, 1H, –OH); 8.95 (s, 1H, –CH=N–); 6.98 (d, 3H), 7.41 (m, 4H), 7.67 (d, 1H) (aromatic); 5.05 (s, 2H, –CH₂–).

2.3.2. Preparation of OV(IV)-Y (oxovanadium exchanged zeolite)

A filtered solution of $VOSO_4 \cdot 5H_2O$ (3.0 g, 12 mmol) dissolved in 50 ml of distilled water was added to a suspension of Na-Y zeolite (5.0 g) in 300 ml of distilled water and the reaction mixture was heated at 90 °C with stirring for 24 h. The light green solid was filtered, washed with hot distilled water until filtrate was free from any vanadyl ion content, and dried at 150 °C for 24 h.

2.3.3. Preparation of Cu(II)-Y (copper exchanged zeolite)

Cu(II)-Y was prepared following essentially the same procedure outlined for OV(IV)-Y replacing $VOSO_4$ by $Cu(NO_3)_2$.

2.3.4. Preparation of $[V^V O_2(sal-ambmz)]-Y(I)$

A mixture of OV-Y (1.0 g) and Hsal-ambmz (2.5 g) was mixed in 100 ml of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was suction filtered and then extracted with methanol using Soxhlet extractor until the complex was free from unreacted ligand. The solid was further suspended in methanol and oxidized by passing air while stirring at room temperature for 24 h. After filtering, the uncomplexed vanadium(IV/V) ions present in the zeolite was removed by stirring with aqueous 0.01 M NaCl solution for 8 h. Finally the resulting solid was washed with water until free from chloride ions and dried at 120 °C for several hours to constant weight.

2.3.5. Preparation of $[Cu^{II}(sal-ambmz)Cl]-Y(2)$

A methanolic solution of Hsal-ambmz (2.5 g in 50 ml) was added to Cu-Y suspended in 50 ml of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The

resulting material was filtered off and extracted with methanol till the complex was free from unreacted Hsal-ambmz. The uncomplexed Cu(II) ion present in the zeolite-Y was removed by stirring with aqueous 0.01 M NaCl solution for 8 h. It was filtered, washed with distilled water till no trace of chloride ion and dried at 120 °C for several hours to constant weight.

2.3.6. Preparation of $[V^VO_2(\text{sal-ambmz})](3)$

This complex was prepared following the procedure reported in the literature [31]. Yield 75%. Anal. found: C, 53.76%; H, 3.76%; N, 12.42%. Calcd. for $C_{15}H_{12}N_3O_3V$ (333.22): C, 54.07%; H, 3.63%; N, 12.61%. 1H NMR (DMSO- d_6 , δ /ppm): 9.10 (s, 1H, $-\text{CH}=\text{N}-$); 6.86 (d, 3H), 7.38 (s, 1H), 7.50 (t, 1H), 7.60 (d, 1H), 7.66 (d, 1H), 8.10 (d, 1H) (aromatic); 5.52 (s, 2H, $-\text{CH}_2-$).

2.3.7. Preparation of $[\text{Cu}^{II}(\text{sal-ambmz})\text{Cl}](4)$

A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.852 g, 5 mmol) dissolved in methanol (20 ml) was added to a hot solution of Hsal-ambmz (1.26 g, 5 mmol) in 30 ml of methanol, and the reaction mixture was refluxed on a water bath for 5 h. Green solid of $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ slowly separated out within a few hours period on cooling the solution to ambient temperature. This was filtered off, washed with methanol and dried. Yield 68%. Anal. found: C, 50.72%; H, 3.92%; N, 12.23%. Calcd. for $C_{15}H_{12}N_3\text{OCu}$ (368.33): C, 51.38%; H, 3.71%; N, 11.99%.

2.4. Catalytic activity study

2.4.1. Oxidation of phenol

The catalytic hydroxylation of phenol was carried out in a 50 ml flask fitted with a water circulated condenser. In a typical reaction, 30% aqueous H_2O_2 (17.01 g, 0.15 mol) and phenol (4.7 g, 0.05 mol) were mixed in 2 ml of CH_3CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. An appropriate catalyst (0.025 g) was added to the reaction mixture and the reaction was considered to begin. During the reaction, the products were analysed by withdrawing small aliquots after specific interval of time using a gas chromatograph, and confirming the identity by GC–MS. The effects of various parameters, such as amounts of oxidant, and catalyst as well as the temperature of the reaction were studied in order to see their effect on the conversion and selectivity of the reaction products.

2.4.2. Oxidation of styrene

Styrene (0.50 g, 0.005 mol), aqueous 30% H_2O_2 (1.70 g, 0.015 mol) and catalyst (15 mg) were taken in 10 ml of CH_3CN and the reaction was carried out at 75 °C. The progress of the reaction was monitored as mentioned above and identity of various products confirmed by GC–MS.

2.4.3. Oxidation of methyl phenyl sulfide

Methyl phenyl sulfide (0.62 g, 0.005 mol) was dissolved in 20 ml of acetonitrile. After addition of H_2O_2 (0.57, 0.005 mmol) and catalyst (5 mg), the reaction mixture was stirred at room temperature for 2 h. During the reaction, the reaction products

formed were analysed using gas chromatograph by withdrawing small aliquots after specific interval of time. The identities of the products were confirmed by GC–MS.

3. Results and discussion

3.1. Characterisation of catalysts

Synthesis of metal complexes encapsulated in the nano-cavity of zeolite-Y involves two steps: (i) exchange of VO(IV) and Cu(II) ions with NaY in aqueous solution and (ii) reaction of metal exchanged zeolites, i.e. OV(IV)-Y and Cu(II)-Y with excess Hsal-ambmz in methanol where ligand slowly enters into the cavity of zeolite-Y due to its flexible nature and interacts with metal ions. This method has been described as flexible ligand method [14,22]. Soxhlet extraction using methanol finally purified the impure complexes. In case of vanadium complex, initially formed oxovanadium(IV) species slowly oxidizes by air in solution to give dioxovanadium(V) complex $[\text{VO}_2(\text{sal-ambmz})]$. The remaining uncomplexed metal ions in zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. As one extra anionic ligand would be required to balance the overall charges on the Cu(II), Cl^- of NaCl used during exchanged process fulfills this requirement. Thus, the formula of copper(II) complex may be written as $[\text{Cu}(\text{sal-ambmz})(\text{Cl})]-\text{Y}$. The percentage of metal contents determined before and after encapsulation by inductively coupled plasma (ICP; Labtam 8440 plasma lab), along with their expected formula and color are presented in Table 1. As crude mass was extracted with methanol, the metal ion content found after encapsulation is only due to the presence of metal complexes in the super cages of the zeolite-Y. The molecular formula of the complexes are based on the neat complexes $[\text{VO}_2(\text{sal-ambmz})]$ and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ that have also been prepared and characterized.

3.2. 3D molecular structure

A C.S. Chem Ultra molecular modeling and analysis programme [36] was used to create three-dimensional model structure for $[\text{VO}_2(\text{sal-ambmz})]$. Fig. 1 presents the molecular structure, and the selected bond lengths and bond angles are given along with the figure's caption. Complex $[\text{VO}_2(\text{sal-ambmz})]$ represents the distorted trigonal pyramid where phenolate-O (O9) and the benzimidazole-N (N21) are in the axial position ($\angle\text{O9}-\text{V12}-\text{N21} = 168.098^\circ$). The azomethine-N and the two doubly bonded oxygen atoms are in the trigonal plane. Similar structure for a closely related complex $[\text{VO}_2(\text{sal-aebmz})]$ (Hsal-aebmz = Schiff base derived from

Table 1
Chemical composition, physical and analytical data

No.	Catalyst	Color	Metal content (wt.%)
1	OV-Y	Light green	4.58
2	$[\text{VO}_2(\text{sal-ambmz})]-\text{Y}$	Light cream	1.82
3	Cu-Y	Pale blue-green	7.60
4	$[\text{Cu}(\text{sal-ambmz})\text{Cl}]-\text{Y}$	Pale brown	2.57

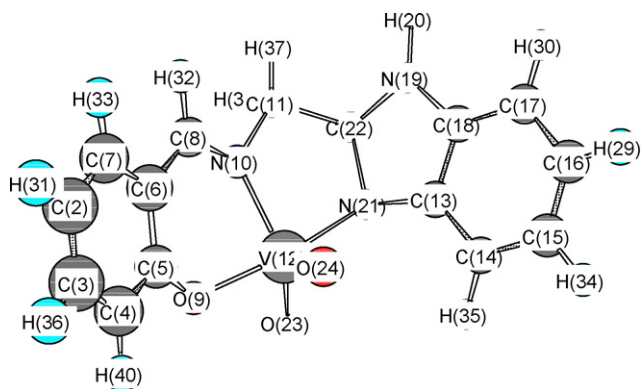


Fig. 1. 3D model structure of $[\text{VO}_2(\text{sal-ambmz})]$. Bond length (Å): V–O(9), 1.873; V–N(10), 1.910; V–N(21), 1.918; V–O(23), 1.868; V–O(24), 1.865. Bond angle ($^\circ$): O(9)–V–N(21), 168.098; O(9)–V–N(10), 88.017; N(10)–V–N(21), 84.702; N(10)–V–O(23), 123.633; N(10)–V–O(24), 107.407; N(21)–V–O(23), 87.666; N(21)–V–O(24), 97.091; O(23)–V–O(24), 128.959.

salicylaldehyde and 2-aminoethylbenzimidazole) has been structurally characterized by single crystal X-ray study [31].

Most $[\text{Cu}(\text{ONN})\text{X}]$ (where ONN = coordinating atoms of monobasic ligands, $\text{X} = \text{Cl}^-$, Br^- , N_3^- etc.) type complexes exist as dimer/polymer where each unit has square pyramidal structure through bridging of X^- [37–39]. Complex $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ may also exist as dimer/polymer. However, such dimeric/polymeric structure will not be possible for the complex $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ encapsulated in zeolite-Y due to space constraint. As spectral patterns of neat as well as encapsulated complexes (vide infra) are same, a square planar structure may also be suggested for encapsulated complexes and this is possible only on additional coordination of, e.g. water with Cu(II). Therefore, no attempt has been made to give three dimensional model structure for the neat complex $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$.

3.3. Scanning electron micrograph study

The scanning electron micrographs (SEM) of the metal exchanged zeolite and their respective encapsulated complexes indicate the presence of well defined crystals free from any shadow of the metal ions or complexes present on their external surface. The representative micrographs of OV(IV)-Y and $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ are presented in Fig. 2.

3.4. Thermogravimetric analysis

The thermal decomposition of catalysts $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ (1) and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ (2) usually occurs in two major steps. An endothermic weight loss of ca. 4% (in 1) or ca. 7% (in 2) occurs in the temperature range 150–250 $^\circ\text{C}$ which is possibly due to the removal of intrazeolite water. The second step of exothermic weight loss consists of several sub-steps and starts immediately after first step and continue till 800 $^\circ\text{C}$ to constant weight. A weight loss of ca. 7% (in 1) or ca. 10% (in 2) due to the slow decomposition of metal complexes is expected in this wide temperature range. The loss in small percentage indicates the insertion of only small amount of metal complexes in the cavity

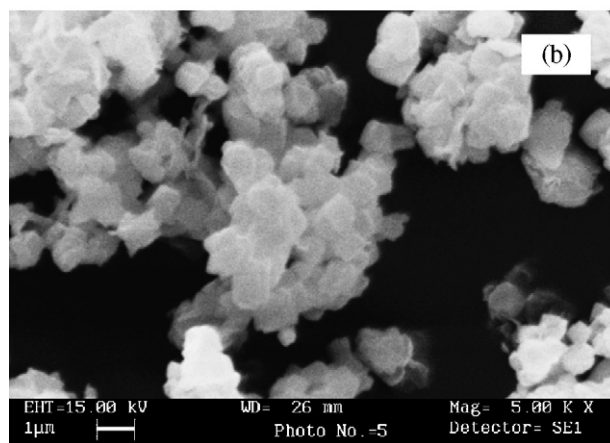
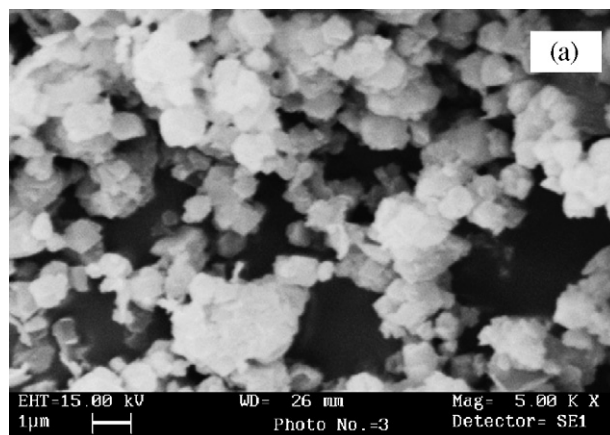


Fig. 2. Scanning electron micrograph of (a) OV(IV)-Y and (b) $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$.

of the zeolite-Y. This is in agreement with the low percentage of metal content obtained for encapsulated complexes.

3.5. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na-Y, OV(IV)-Y, Cu(II)-Y, $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ were recorded at 2θ values between 5 and 70 to see their crystalline nature and to ensure encapsulation of complexes inside the cavity. The XRD patterns of Na-Y, Cu(II)-Y and encapsulated complex $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ are presented in Fig. 3. An essentially similar pattern in Na-Y, metal exchanged zeolite-Y and metal complex encapsulated zeolite-Y was noticed, though slight change in the intensity of the bands in later two cases were in order. These observations indicate that the framework of the zeolite has not undergone any significant structural change during incorporation of the catalysts. This is further, in consultation with SEM, suggests that the crystallinity of the zeolite-Y is preserved during encapsulation. No new peaks could be detected in metal exchanged or complex encapsulated zeolite samples probably due to poor loading of these in zeolite framework.

3.6. IR spectral studies

A partial list of IR spectral data is presented in Table 2. IR spectrum of ligand exhibits two sharp bands at 1617 and

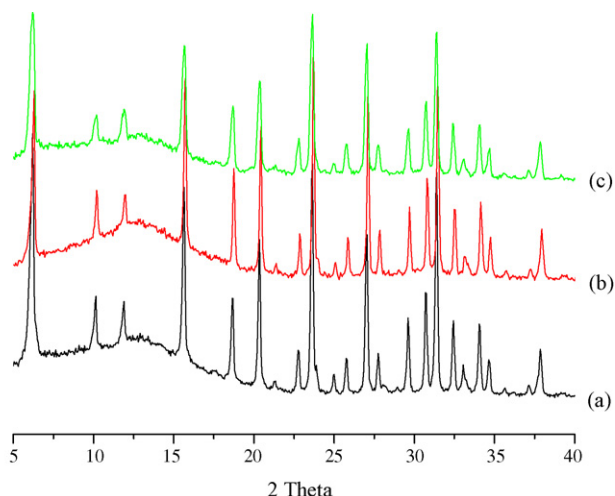


Fig. 3. XRD pattern of Na-Y (a), Cu-Y (b) and [Cu(sal-ambmz)Cl]-Y (c).

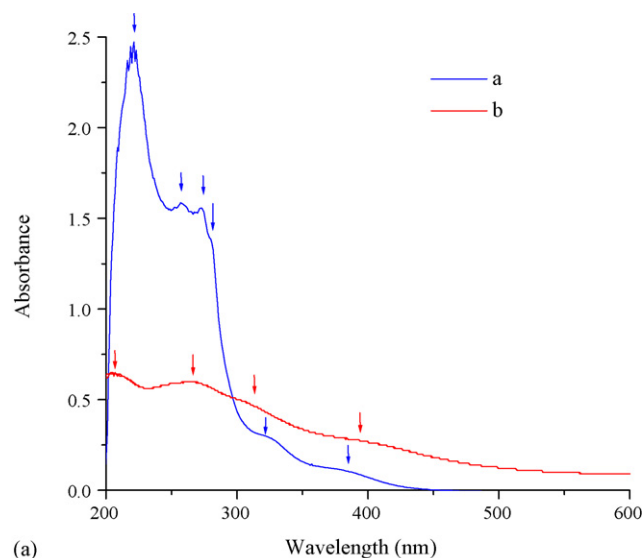
1634 cm^{-1} due to $\nu(\text{C}=\text{N})$ (azomethine/ring) stretch. These bands move towards lower wave numbers on coordination of azomethine/ring nitrogen to the metal. The presence of hydrogen bonding between NH of benzimidazole and other electronegative atoms in ligand is indicated by the appearance of several medium intensity band in the range 2500–2700 cm^{-1} . These bands are also present in complexes indicating the presence of hydrogen bonding in complexes. The coordination of the phenolic oxygen could not be ascertained unequivocally due to the appearance of strong band in the ca. 3400 cm^{-1} . However, in the light of structurally characterized complex, e.g. [VO₂(sal-aebmz)](Hsal-aebmz = Schiff base derived from salicylaldehyde and 2-aminoethylbenzimidazole), a monobasic tridentate ONN behaviour of the ligand may also be considered here [31]. Location of bands due to *cis*-VO₂ structure in zeolite encapsulated vanadium complex has not been possible due to appearance of a strong and broad band at ca. 1000 cm^{-1} due to zeolite framework; neat complex [VO₂(sal-ambmz)] exhibits two bands at 940 and 908 cm^{-1} .

3.7. Electronic spectral studies

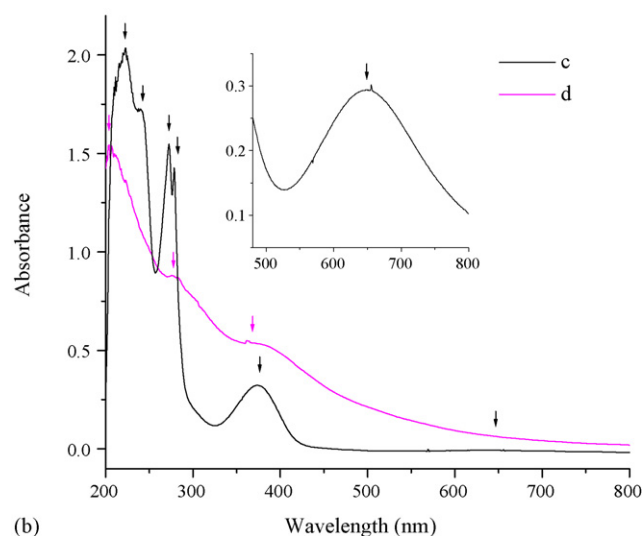
Table 2 also presents electronic spectral data of ligand and complexes. The electronic spectral studies of ligand Hsal-ambmz and its dioxovanadium(V) complex [VO₂(sal-ambmz)] have been discussed in detail [31]. Similar spectral patterns were observed with neat as well as encapsulated vanadium complexes;

Table 2
IR and electronic spectral data of ligand, pure and encapsulated complexes

Compound	IR (cm^{-1}), $\nu(\text{C}=\text{N})$ (azomethine/ring)	λ_{max} (nm)
Hsal-ambmz	1636, 1617	207, 256, 274, 281, 324
[VO ₂ (sal-ambmz)]-Y	1625, 1600	207, 267, 314, 395
[Cu(sal-ambmz)Cl]-Y	1633, 1536	204, 276, 367
[VO ₂ (sal-ambmz)]	1624, 1599	218, 257, 274, 281, 320, 384
[Cu(sal-ambmz)Cl]	1634, 1600	221, 240, 272, 278, 374, 645



(a)



(b)

Fig. 4. Electronic spectra of [VO₂(sal-ambmz)] (a) and [VO₂(sal-ambmz)]-Y (b). Electronic spectra of [Cu(sal-ambmz)Cl] (c) and [Cu(sal-ambmz)Cl]-Y (d).

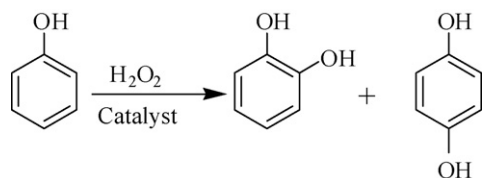
Fig. 4a. Encapsulated as well as neat copper complexes also exhibit similar spectral patterns in the UV region. Additional band at ca. 645 nm was observed in neat [Cu(sal-ambmz)Cl] due to d–d transition; Fig. 4b.

3.8. Catalytic activity

3.8.1. Oxidation of phenol

Oxidation of phenol, catalysed by [VO₂(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y was carried out using H₂O₂ as an oxidant and as expected, based on directing group of phenol, two major products, i.e. catechol and hydroquinone as shown by Scheme 1 were identified from the reaction mixture.

In order to achieve suitable reaction conditions for the maximum oxidation of phenol, the effect of following reaction parameters were studied in detail using [VO₂(sal-ambmz)]-Y as a representative catalyst:



- H_2O_2 concentration (moles of H_2O_2 per mole of phenol);
- amount of catalyst per mole of phenol;
- temperature.

The results of all these studies and possible explanations are summarized below.

The effect of H_2O_2 concentration on the oxidation of phenol is illustrated in Fig. 5. Four different H_2O_2 /phenol molar ratios, viz. 1:1, 2:1, 3:1 and 4:1 were considered while keeping the fixed amounts of phenol (4.7 g, 0.05 mol) and catalyst (25 mg) in 2 ml of MeCN and the reaction was carried out at 75°C . It is clear from the plot presented as a function of time that the 3:1 molar ratio is best ratio to obtain the phenol conversion of 42.5% at 75°C while 2:1 and 1:1 gave lower conversions. About 6 h was required to establish the equilibrium. Though, H_2O_2 /phenol molar ratio of 4:1 gives relatively higher conversion, the selectivity of H_2O_2 would go considerably low. Induction period of ca. 1 h in each plot suggests that either formation of the reactive intermediate takes longer time itself or intermediate formed takes longer time to transfer oxygen to the substrate.

Similarly, for phenol (4.7 g, 0.05 mol), H_2O_2 (17.01 g, 0.15 mol) and acetonitrile (2 ml), four different amount of catalyst, viz. 15, 25, 50 and 75 mg were considered and the reactions were monitored at 75°C . Results illustrated in Fig. 6 for the oxidation of phenol shows that 15 mg catalyst gives only 38.6% conversion, while 25 mg catalyst is sufficient enough to obtain 42.5% phenol conversion at 75°C in 6 h of reaction time. Further increments of catalyst hardly improve the conversion. This

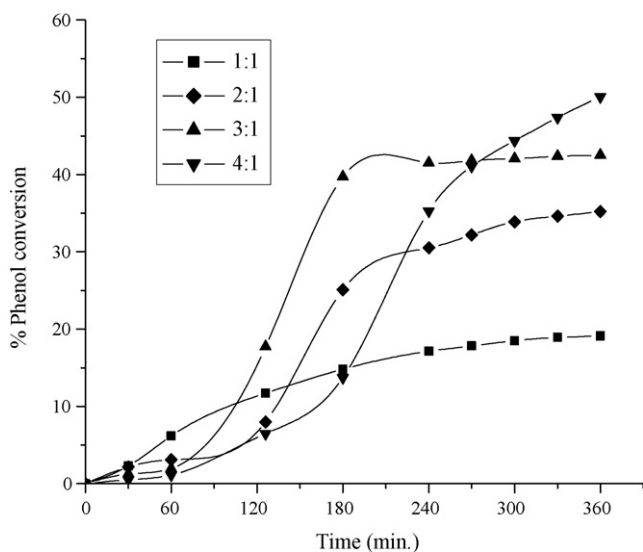


Fig. 5. Effect of H_2O_2 concentration (H_2O_2 : phenol) on phenol oxidation.

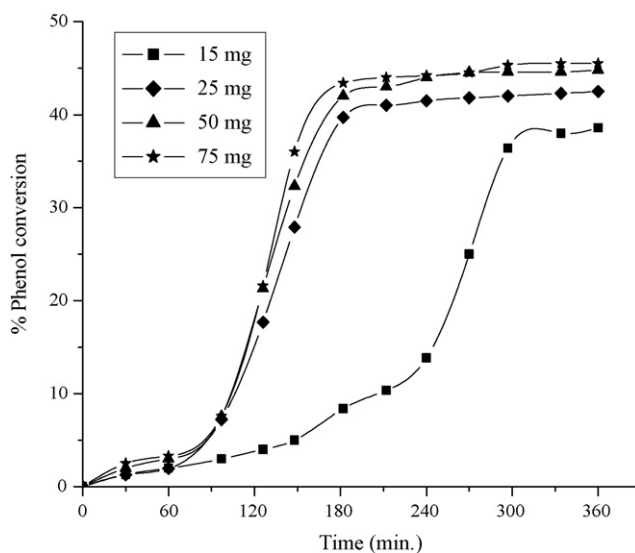


Fig. 6. Effect of amount of catalyst per unit weight of phenol.

has been interpreted in terms of the thermodynamic and mass transfer limitations at higher reaction rates.

The temperature of the reaction medium also influences the reaction rate. It has been inferred that 80°C is the best suited temperature for the maximum oxidation of phenol. At this temperature, a maximum of 43.9% conversion was achieved in 6 h of contact time when phenol (4.7 g, 0.05 mol), H_2O_2 (17.01 g, 0.15 mol) and $[\text{VO}(\text{sal-ambmz})]$ (25 mg) were taken in 2 ml of acetonitrile. As shown in Fig. 7, running the reaction at lower temperature, viz. 70°C and 75°C lower the conversion.

Thus, optimised operating reaction conditions for the maximum oxidation of phenol were fixed as follows: phenol (4.7 g, 0.05 mol), H_2O_2 (17.01 g, 0.15 mol), catalyst (25 mg), CH_3CN (2 ml) and temperature (80°C). Under this condition, the performances of other catalysts were studied and the percentages of phenol oxidation after 6 h of reaction time

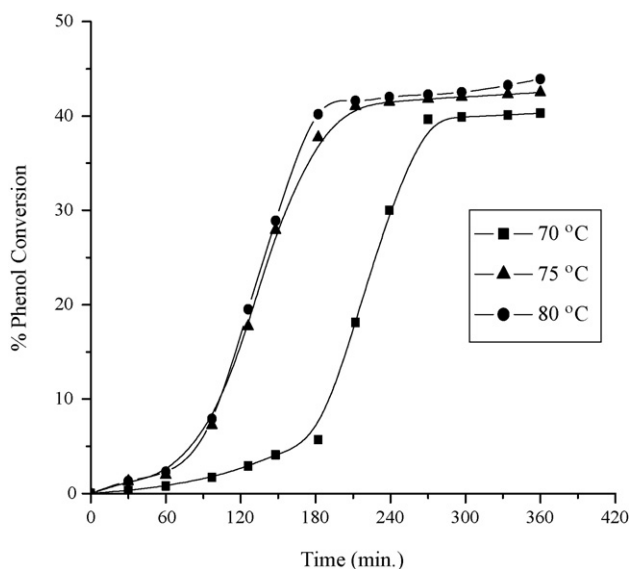


Fig. 7. Effect of temperature on the oxidation of phenol.

Table 3

Percentage conversion of phenol along with TOF values and the selectivity of the products formed after 6 h of reaction time

Catalyst	% conversion	TOF ^a (h ⁻¹)	% selectivity	
			Catechol	Hydroquinone
[VO ₂ (sal-ambmz)]-Y	43.9	409.6	65.2	34.8
[Cu(sal-ambmz)Cl]-Y	42.0	565.7	73.9	26.1
[VO ₂ (sal-ambmz)]	37.6	167.1	71.4	28.6
[Cu(sal-ambmz)Cl]	35.4	477.9	68.8	31.2

^a TOF (turn over frequency) moles of substrate converted per mole of metal (in the solid state catalyst) per hour.

along with the products selectivity are presented in Table 3 and the conversion plotted as a function of time is presented in Fig. 8. With 42.0% conversion of phenol, [Cu(sal-ambmz)Cl]-Y exhibits nearly identical potentiality to that of [VO₂(sal-ambmz)]-Y. However, the order of the percent conversion is: [VO₂(sal-ambmz)]-Y (43.9%) > [Cu(sal-ambmz)Cl]-Y (42.0%). Amongst the products formed, the selectivity of catechol is better and varies between 65.2 and 73.9%, while that of hydroquinone between 26.1 and 34.8%. The performances of neat complexes [VO₂(sal-ambmz)] and [Cu(sal-ambmz)Cl] under the above reaction conditions are also good and the conversions follow the order: [VO₂(sal-ambmz)] (37.6%) > [Cu(sal-ambmz)Cl] (35.4%). However, the overall performance of encapsulated complexes is better than the corresponding neat ones. The turn over frequencies (TOF) of the encapsulated complexes are also higher.

The catalytic performances of these encapsulated complexes compare well with the data reported in the literature. For example, the observed conversions for zeolite-Y encapsulated complexes [Cu(salpn)]-Y (H₂salpn = *N,N'*-bis(salicylidene) propane-1,3-diamine) (31%) [40], Cu(saldien)]-Y (46%) [41], [VO(salen)]-Y (32.6%) [25] are close to the one reported in Table 3. Catalyst NH₄[VO(sal-inh)]-Y (H₂sal-inh = Schiff base derived from salicylaldehyde and iso nicotinic acid hydrazide)

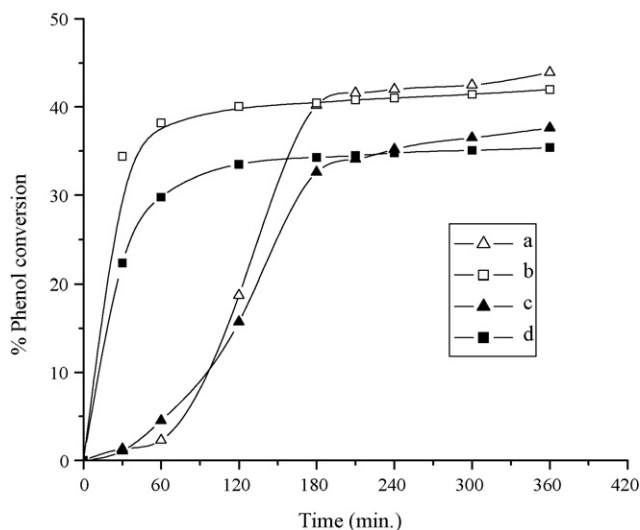
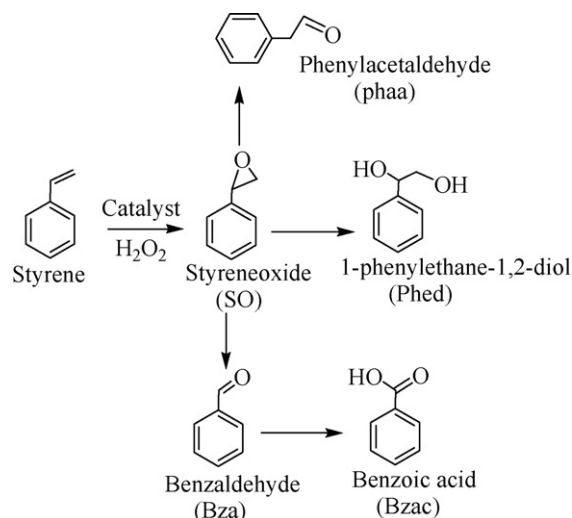


Fig. 8. Effect of catalysts, [VO₂(sal-ambmz)]-Y (a), [Cu(sal-ambmz)Cl]-Y (b), [VO₂(sal-ambmz)]-Y (c) and [Cu(sal-ambmz)Cl] (d) on the oxidation of phenol.



Scheme 2.

exhibits only 26.5% conversion [42]. However, selectivity towards the formation of catechol for complexes reported here is less (65.2–73.9%) than the reported value of ca. 90%.

3.8.2. Oxidation of styrene

[VO₂(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y also catalyse the oxidation of styrene in presence of H₂O₂ and give styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde along with only minor amounts of unidentified products. Scheme 2 represents the formation of all these products. These identified products are common and are observed by others as well [27–31].

In order to achieve suitable reaction conditions for a maximum oxidative conversion of styrene, [VO₂(sal-ambmz)]-Y was taken as a representative catalyst and three different parameters, viz. amount of oxidant and catalyst were varied. The effect of H₂O₂ concentration on the oxidation of styrene is illustrated in Fig. 9. At a styrene to 30% H₂O₂ molar ratio of 1:1, a

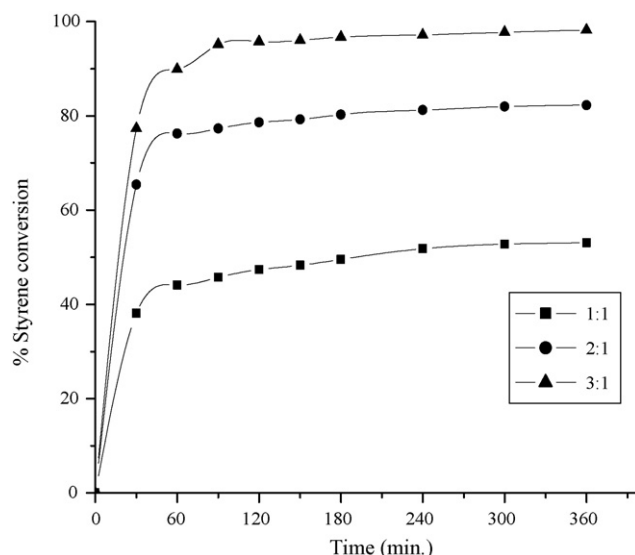


Fig. 9. Effect of H₂O₂ concentration (H₂O₂: styrene) on oxidation of styrene.

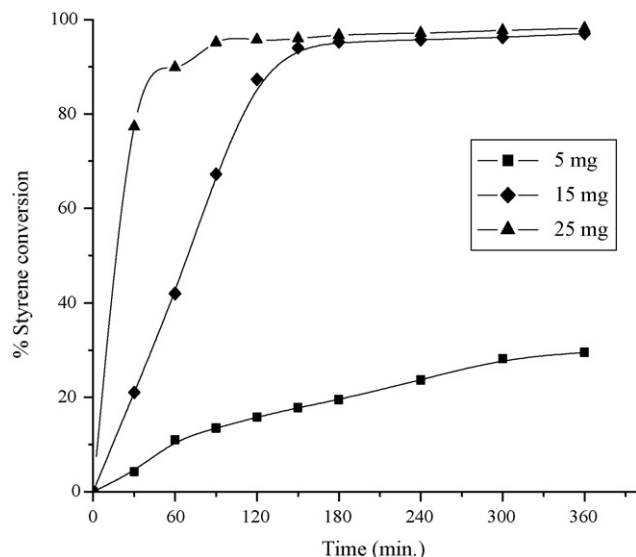


Fig. 10. Effect of amount of catalyst per unit weight of styrene.

maximum of 53.1% conversion was achieved in 6 h of contact time for styrene (5 mmol), $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ (15 mg), 30% H_2O_2 (0.57 g, 0.005 mol), acetonitrile (10 ml) and temperature (75°C). Increasing the ratio to 1:2 improved the conversion to 82.3%, while 1:3 ratio has shown a maximum of 98.2% conversion. Further increment of H_2O_2 shows no improvement in conversion.

Similarly for three different amounts (viz. 5, 15, and 25 mg) of catalyst and H_2O_2 to styrene molar ratio of 3:1 under above reaction conditions, 5 mg gave only 29.5% oxidative conversion while 15 and 25 mg have shown nearly identical results with ca. 97% conversion in 6 h of contact time; Fig. 10. Thus, 15 mg catalyst may be considered sufficient enough to run the reaction under above conditions.

After acquiring the optimised reaction conditions for $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$, catalyst $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ was also tested under the same reaction conditions. Thus, for 5 mmol of styrene, 15 mmol of 30% H_2O_2 and 15 mg of $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ were taken in 10 ml of CH_3CN and the reaction was carried out at 75°C . Analysis after 6 h of reaction time showed 63.4% conversion which is less than that observed for $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$. Catalytic activity of neat complexes $[\text{VO}_2(\text{sal-ambmz})]$ and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ have also been carried out. Fig. 11 provides percentage conversion of styrene as a function of time for various catalysts. A comparative report dealing with the conversion of styrene and selectivity of various

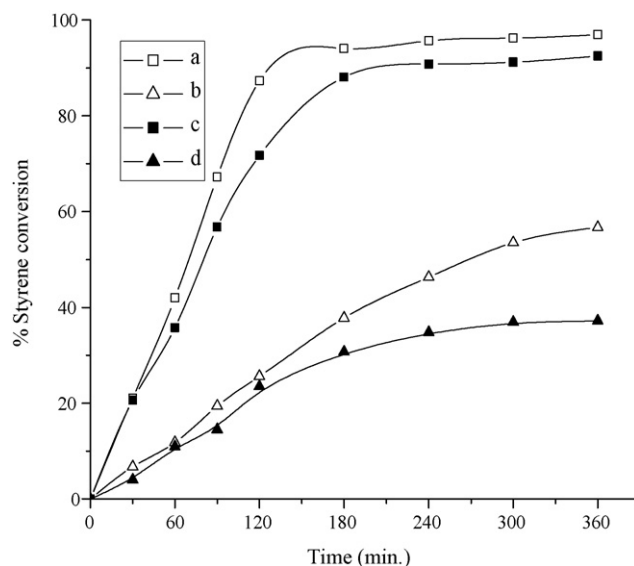


Fig. 11. Effect of $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ (a), $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ (b), $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ (c) and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ (d) on the oxidation of styrene.

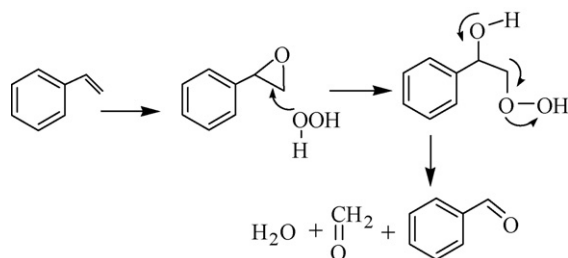
products are summarized in Table 4. It is clear from the table that neat complex $[\text{VO}_2(\text{sal-ambmz})]$ exhibits 92.5% conversion of styrene in 6 h which is equally good to that of respective encapsulated one, while $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ registers only 37.2% conversion which is much less than the respective encapsulated one. The turn over rates calculated for these neat complexes are 68.4 and 83.6, respectively. These values are less than that observed for encapsulated complexes. Moreover, the recycle ability, easy recovery of the encapsulated catalysts and almost no leaching of complexes during reaction make them better catalysts over the neat ones.

Independent of the type of catalyst, the selectivity of various reaction products follow the order: benzaldehyde > 1-phenylethane-1,2-diol > benzoic acid > styrene oxide > phenyl acetaldehyde. The formation of an important component styrene oxide is low in all cases. A highest yield of benzaldehyde is possibly due to further oxidation of styrene oxide formed in the first step by a nucleophilic attack of H_2O_2 on styrene oxide followed by cleavage of the intermediate hydroperoxystyrene, Scheme 3 [29]. The formation of benzaldehyde may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via a radical mechanism. High amount of water present in H_2O_2 is partly responsible for the possible hydrolysis of styrene oxide to 1-phenylethane-1,2-diol. Other products, e.g. benzoic acid formation through further oxidation of benzaldehyde is not so

Table 4
Products selectivity and percent conversion of styrene after 6 h of reaction time

Catalyst	% conversion	TOF (h^{-1})	% selectivity ^a					
			SO	BzA	PhED	BzAc	PhAA	Other
$[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$	97.0	150.9	5.4	54.9	25.3	13.2	0.2	1.0
$[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$	56.7	127.4	5.6	51.1	6.3	19.9	13.2	3.5
$[\text{VO}_2(\text{sal-ambmz})]$	92.5	68.4	6.8	56.2	23.2	11.6	1.7	0.5
$[\text{Cu}(\text{sal-ambmz})\text{Cl}]$	37.2	83.6	4.2	63.1	12.8	11.5	4.6	3.8

^a SO: styrene oxide; BzA: benzaldehyde; PhED: 1-phenylethane-1,2-diol; BzAc: benzoic acid; PhAA: phenyl acetaldehyde.



high in all reactions. Similarly the formation of phenylacetaldehyde through isomerisation of styrene oxide is less in all cases.

Catalytic potential of these complexes cannot be compared directly with similar complexes due to limited literature. Zeolite-Y encapsulated catalyst [Mn(salen)]-Y exhibits ca. 30% conversion of styrene using molecular oxygen as an oxidant in excess of *tert*-butylhydroperoxide as initiator [43]. About 80% conversion of styrene was noted with polymer supported catalyst PS-K[VO₂(sal-ohyba)] (H₂sal-ohyba = Schiff base derived from salicylaldehyde and *o*-hydrobenzylamine). The selectivity of styrene oxide in all these catalysts is always low [44].

3.8.3. Oxidation of methyl phenyl sulfide (thioanisol)

The sulfur atom of the methyl phenyl sulfide is electron rich and has been shown to undergo electrophilic oxidation to give sulfoxide. Such oxidation of methyl phenyl sulfide was tested using [VO₂(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-Y as catalyst. Using the fixed amount of methyl phenyl sulfide (0.62 g, 0.005 mol), catalyst [VO₂(sal-ambmz)]-Y (15 mg) and H₂O₂ (0.285 g, 0.0025 mol) in 20 ml of CH₃CN and running the reaction at room temperature gave 47.1% conversion with a mixture of two products, methyl phenyl sulfoxide and methyl phenyl sulfone, Scheme 4. Increasing the oxidant amount to 0.005 mol, i.e. at 1:1 substrate to oxidant molar ratio, this conversion reached to 97.3% within 2 h of contact time. The results obtained and reaction conditions used suggested using substrate to oxidant ratio of 1:1 to obtain the maximum oxidation of methyl phenyl sulfide oxidation.

In order to optimise the amount of catalyst under above operating conditions, four different amounts of catalyst (viz. 1, 5, 10 and 15 mg) were considered and the results obtained are presented in Fig. 12. It turns out from the figure that 5 mg of catalyst was sufficient enough to give a maximum of 96.1% conversion of methyl phenyl sulfide with the percent selectivity for methyl phenyl sulfoxide of 97.1 and methyl phenyl sulfone of 2.9. Increasing the amount to 10 and 15 mg marginally affect the conversion as well selectivity. Under similar conditions neat complex [VO₂(sal-ambmz)] gave a maximum conversion of 91% where selectivity of major product was 98%.

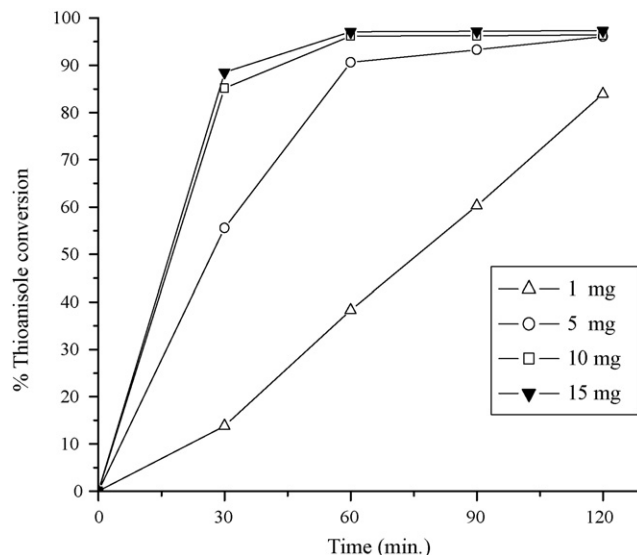
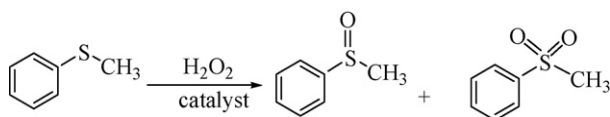


Fig. 12. Effect of catalyst weight on thioanisol oxidation.

Thus, neat as well as encapsulated complexes both are highly selective towards sulfoxide formation. A blank reaction under similar conditions, i.e. methyl phenyl sulfide (0.005 mol), H₂O₂ (0.005 mmol) and CH₃CN (20 ml), resulted in 37% conversion of methyl phenyl sulfide, where 69.3% selectivity was registered for sulfoxide and 30.7% for sulfone. Thus, these complexes not only enhance the percent conversion of methyl phenyl sulfide, they also improve the selectivity for sulfoxide. However, encapsulated complex may be considered as better catalyst as recovery of the catalyst becomes easier and its turn over rate is also high in comparison to the neat one. Table 5 summarizes products selectivity and conversion details. On the contrary, neat as well as encapsulated copper complexes do not affect the conversion of methyl phenyl sulfide and thus they are catalytically inactive for sulfide oxidation.

3.8.4. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the neat complexes were treated with H₂O₂ and progress of the reaction was monitored by electronic absorption spectroscopy; Fig. 13. Thus, the titration of methanolic solution of [VO₂(sal-ambmz)] with one-drop portions of 30% H₂O₂ dissolved in methanol resulted in the gradual shift of 384 nm band to 380 nm along with the decrease in band maximum while band at 320 nm recorded only increase in intensity. Other two bands appearing at 274 and 281 nm showed very slight increase in intensity. The UV band at 257 nm showed trend of increasing intensity only and

Table 5
Percent conversion of thioanisol and selectivity of sulfoxide and sulfone formation at room temperature after 2 h of contact time

Catalyst (5 mg)	% conversion	TOF h ⁻¹	% selectivity	
			Sulfoxide	Sulfone
[VO ₂ (sal-ambmz)]-Y	96.1	1345.2	97.1	2.9
[VO ₂ (sal-ambmz)]	91.0	151.6	98.0	2.0
Without catalyst	37.0	–	69.3	30.7

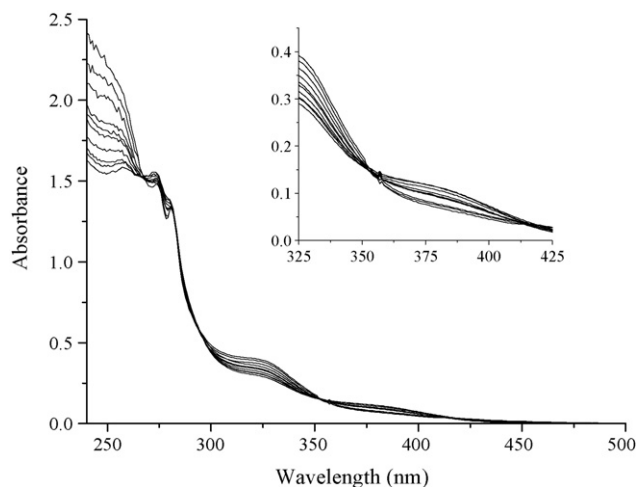


Fig. 13. Titration of $[\text{VO}_2(\text{sal-ambmz})]$ with H_2O_2 .

finally disappeared. We interpret these changes due to the formation of oxoperoxovanadium(V) complex $[\text{VO}(\text{O}_2)(\text{sal-ambmz})]$. Such oxoperoxovanadium(V) complexes with, e.g. Hsal-aebmz, a closely related ligand, has been prepared and characterized. The final spectral pattern of $[\text{VO}_2(\text{sal-ambmz})]$ is also similar to the known complex $[\text{VO}(\text{O}_2)(\text{sal-aebmz})]$ [31]. Thus, the formation of an intermediate oxoperoxovanadium(V) complex may be proposed which finally transfers oxygen to the substrates.

The addition of one-drop portions of 30% H_2O_2 dissolved in methanol to a methanolic solution of $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ resulted in the quick reduction in the intensity of d–d band at 645 nm without changing its position followed by a slow increase in band maximum on further addition of H_2O_2 . The band at 374 nm experienced decrease in intensity, while a shoulder appearing at 298 nm slowly disappeared. Other two bands at 278 and 271 nm slowly gained intensity, and the band at 240 nm gained intensity but finally disappeared. Fig. 14 presents spectral changes observed. All these suggest the interaction of H_2O_2 with Cu(II) centre.

At least three types of intermediates having copper–oxygen interaction, viz. side-on $\text{Cu}^{\text{III}}-(\mu-\eta^2\text{-peroxo})-\text{Cu}^{\text{III}}$, bis(μ -oxo-

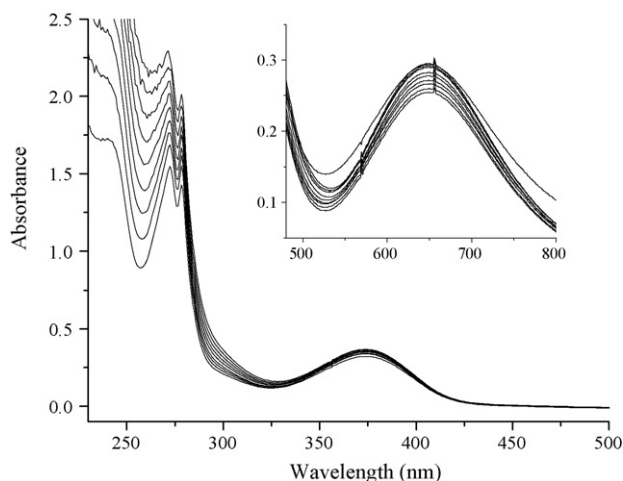


Fig. 14. Titration of $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ with H_2O_2 .

Cu^{III}) and $\text{Cu}^{\text{III}}-\text{O}-\text{O}-\text{H}$ (copper–hydroperoxide) have been reported in the literature during catalytic action [45]. The facile formation of $[(\text{HOO})-\text{Cu}(\text{sal-ambmz})\text{Cl}]$ intermediate is expected in zeolite-encapsulated copper complex as only monomeric species is present in the cavity. A quick decrease in the intensity of 645 nm band may be due to interaction of H_2O_2 to $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ while increment in intensity of 271 and 278 nm bands may possibly be due to the formation of hydroperoxide $[(\text{HOO})-\text{Cu}(\text{sal-ambmz})\text{Cl}]$ intermediate of the neat complex. Hydroperoxocopper complexes are known to exhibit a charge transfer band at ca. 600 nm [46]. The decrease in intensity of 645 nm band without any isosbestic point in neat complex may possibly be due to the merging of this additional charge transfer band with d–d transition. The intermediate finally transfers coordinated oxygen atoms to the substrates to give the products. Thus, the catalytic performance of encapsulated catalyst could be attributed to the formation of facile and reversible intermediate species.

3.8.5. Test for recycle ability and heterogeneity of the reactions

The recycle ability of both the encapsulated complexes has been tested in all three catalytic reactions. In a typical experiment, e.g. for styrene, the reaction mixture after a contact time of 6 h was filtered and after activating the catalyst by washing with acetonitrile and drying at ca. 120 °C, it was subjected to further catalytic reaction under similar conditions. No appreciable loss in catalytic activity suggests that complex is still present in the cavity of the zeolite-Y. The filtrate collected after separating the used catalyst was placed into the reaction flask and the reaction was continued after adding fresh oxidant for another 4 h. The gas chromatographic analysis showed no improvement in conversion and this confirms that the reaction did not proceed upon removal of the solid catalyst. The reaction was, therefore, heterogeneous in nature.

4. Conclusion

Complexes $[\text{VO}_2(\text{sal-ambmz})]$ and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]$ have been encapsulated in the super cages of zeolite-Y. The integrity of encapsulation was confirmed by spectroscopic studies as well as chemical and thermal analysis. These encapsulated complexes are found active for the oxidation of phenol and styrene with good conversion. A maximum of 43.9% of phenol oxidation was observed with vanadium-based catalyst which is followed by copper-based catalyst. However, the copper-based catalyst is more selective (73.9%) towards the formation of catechol than the vanadium-based catalyst (65.2%). The oxidation of styrene gives at least four different products, where expected product styrene oxide was found only in small yield, and the percentage of benzaldehyde was relatively high. Oxidation of methyl phenyl sulfide using zeolite encapsulated vanadium complex was tested first time, to the best of our knowledge, and as high as 96% conversion with 97% selectivity towards methyl phenyl sulfoxide and only 3% towards methyl phenyl sulfone was observed. It is concluded from the catalytic data and turn over frequency

that encapsulated complexes are better catalysts than the neat ones. These catalysts are recyclable without loss of the catalytic potential. They do not leach in any of the catalytic reactions and are heterogeneous in nature.

References

- [1] R. Ando, H. Ono, T. Yagyu, M. Maeda, *Inorg. Chim. Acta* 357 (2004) 817.
- [2] R. Ando, S. Mori, M. Hayashi, T. Yagyu, M. Maeda, *Inorg. Chim. Acta* 357 (2004) 1177.
- [3] M.R. Maurya, I. Jain, S.J.J. Titinchi, *Appl. Catal. A: Gen.* 249 (2003) 139.
- [4] M.R. Maurya, A. Kumar, P. Manikandan, S. Chand, *Appl. Catal. A: Gen.* 277 (2004) 45.
- [5] M.R. Maurya, A. Kumar, *J. Mol. Catal. A: Chem.* 250 (2006) 190.
- [6] D.C. Sherrington, *Pure Appl. Chem.* 60 (1988) 401.
- [7] J.K. Karjalainen, O.E.O. Hormi, D.C. Sherrington, *Molecules* 3 (1998) 51.
- [8] L. Canali, D.C. Sherrington, *Chem. Soc. Rev.* 28 (1999) 85.
- [9] D.C. Sherrington, *Catal. Today* 57 (2000) 87.
- [10] T. Joseph, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 229 (2005) 241.
- [11] T. Joseph, D. Srinivas, C.S. Gopinath, S.B. Halligudi, *Catal. Lett.* 83 (2002) 209.
- [12] G.S. Rafelt, J.H. Clark, *Catal. Today* 57 (2000) 3 (and references there in).
- [13] R.A. Sheldon, I.W.C.E. Arends, A. Dijkstra, *Catal. Today* 57 (2000) 157.
- [14] C.R. Jacob, S.P. Verkey, P. Ratnasamy, *Microporous Mesoporous Mater.* 22 (1998) 465.
- [15] G.J. Hutchings, *Chem. Commun.* (1999) 301.
- [16] M.R. Maurya, S.J.J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* 214 (2004) 257.
- [17] R.A. Sheldon, R.A. Vansnaten, *Catalytic Oxidation, Principles and Applications*, World Scientific, Singapore, 1995.
- [18] M. Taramasso, G. Perego, B. Notari, US Patent 4,410,501 (1983); M. Taramasso, G. Manara, V. Fattore, B. Notari, US Patent 4,666,692 (1987).
- [19] T. Yokoi, P. Wu, T. Tatsumi, *Catal. Commun.* 4 (2003) 11.
- [20] C. Perego, A. Carati, I. Ingallina, M.A. Mantegazza, G. Bellussi, *Appl. Catal. A: Gen.* 221 (2001) 63.
- [21] H. Zhang, X. Zhang, Y. Ding, L. Yan, T. Ren, J. Suo, *New J. Chem.* 26 (2002) 376.
- [22] K.J. Balakus Jr., A.G. Gabriellov, *J. Inclusion Phenom. Mol. Recogn. Chem.* 21 (1995) 159.
- [23] R. Raja, P. Ratnasamy, *Stud. Surf. Sci. Catal.* 101 (1996) 181.
- [24] S. Seelan, A.K. Sinha, D. Srinivas, S. Sivsanker, *Bull. Catal. Soc. India* 1 (2002) 29.
- [25] M.R. Maurya, M. Kumar, S.J.J. Titinchi, H.S. Abbo, S. Chand, *Catal. Lett.* 86 (2003) 97.
- [26] P.P. Knops-Gerrits, D. de Vos, F.T. Starzyk, P.A. Jacobs, *Nature* 369 (1994) 543.
- [27] K. Srinivasan, P. Michaud, J.K. Kochi, *J. Am. Chem. Soc.* 108 (1986) 2309.
- [28] R. Irie, Y. Ito, T. Katsuki, *Syn. Lett.* (1991) 265.
- [29] V. Hulea, E. Dumitriu, *Appl. Catal. A: Gen.* 277 (2004) 99.
- [30] S.B. Kumar, S.P. Mirajkar, G.C.G. Pais, P. Kumar, R. Kumar, *J. Catal.* 156 (1995) 163.
- [31] M.R. Maurya, A. Kumar, M. Ebel, D. Rehder, *Inorg. Chem.* 45 (2006) 5924.
- [32] A. Butler, M.J. Clague, G.E. Meister, *Chem. Rev.* 94 (1994) 625.
- [33] V.M. Dembitsky, *Tetrahedron* 59 (2003) 4701.
- [34] T.S. Smith II, V.L. Pecoraro, *Inorg. Chem.* 41 (2002) 6754.
- [35] D.C. Crans, A.D. Keramidas, S.S. Amin, O.P. Anderson, S.M. Miller, *J. Chem. Soc., Dalton Trans.* (1997) 2799.
- [36] C.S. Chem 3D Ultra Modeling and Analysis, Cambridge, <http://www.cambridgesoft.com>.
- [37] F. Hueso-Ureña, M.N. Moreno-Carretero, A.L. Peñas-Chamorro, J.M. Amigó, V. Estev, T. Debaerdemaeker, *Polyhedron* 18 (1999) 3629.
- [38] N.R. Sangeeta, S. Pal, *Polyhedron* 19 (2000) 1593.
- [39] C. Adhikary, D. Mal, K.-I. Okamoto, S. Chaudhury, S. Koner, *Polyhedron* 25 (2006) 2191.
- [40] M.R. Maurya, S.J.J. Titinchi, S. Chand, *Appl. Catal. A: Gen.* 228 (2002) 177.
- [41] M.R. Maurya, S.J.J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* 201 (2003) 119.
- [42] M.R. Maurya, H. Saklani, A. Kumar, S. Chand, *Catal. Lett.* 93 (2004) 121.
- [43] A. Zsigmond, A. Horvath, F. Notheisz, *J. Mol. Catal. A: Chem.* 171 (2001) 95.
- [44] M.R. Maurya, U. Kumar, P. Manikandan, *Dalton Trans.* (2006) 3561.
- [45] (a) E.I. Solomon, P. Chen, M. Metz, S.-K. Lee, A.E. Palner, *Angew. Chem. Int. Ed.* 40 (2001) 4570; (b) J.P. Klinman, *Chem. Rev.* 96 (1996) 2541.
- [46] K.D. Karlin, J.C. Hayes, Y. Gultneh, R.W. Cruse, J.W. McKown, J.P. Hutchinson, J. Zubieta, *J. Am. Chem. Soc.* 106 (1984) 2121.