

Oxidation of methyl phenyl sulfide, diphenyl sulfide and styrene by oxovanadium(IV) and copper(II) complexes of NS donor ligand encapsulated in zeolite-Y

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Abstract

Encapsulation of oxovanadium(IV) and copper(II) complexes of monobasic bidentate NS donor ligand, 2-mercaptomethylbenzimidazole (Htmbmz) in the cavity of zeolite-Y by flexible ligand method has been described. These complexes have been characterized by various physico-chemical methods. These encapsulated complexes, abbreviated as [VO(tmbmz)₂]-Y and [Cu(tmbmz)₂]-Y, have been used as catalysts for the oxidation of styrene, methyl phenyl sulfide and diphenyl sulfide. Under the optimized reaction conditions, [VO(tmbmz)₂]-Y gave 96.4% conversion of styrene with five oxidation products, styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde. Conversion of styrene with [Cu(tmbmz)₂]-Y is considerably low (36.9%) and gave only four products, styrene oxide, benzaldehyde, benzoic acid and phenylacetaldehyde. In both cases formation of benzaldehyde is relatively high. These catalysts are also very active for the oxidation of methyl phenyl sulfide and diphenyl sulfide. The oxidation of diphenyl sulfide required at least H₂O₂ to diphenyl sulfide molar ratio of 3:1 to give 91.7% conversion in 7 h of reaction time. However, 94.3% conversion of methyl phenyl sulfide has been achieved within 3 h of contact time at substrate to H₂O₂ molar ratio of 1:1. The catalytic activity of neat complexes using similar molar concentration as that used for the encapsulated complexes under above reaction conditions have also been tested for comparison. It has been observed that the corresponding neat complexes have shown equally good catalytic activities. But high turn over frequency and recyclability make the zeolite-Y encapsulated complexes better than their neat analogues.

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Keywords: Zeolite-Y encapsulated metal complexes; Copper(II) complexes; Oxovanadium(IV) complexes; Catalysts; Oxidation of styrene; Oxidation of methyl phenyl sulfide; Oxidation of diphenyl sulfide

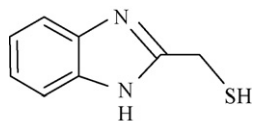
1. Introduction

Oxidation of sulfides (thioethers) to sulfoxides, i.e. sulfoxidases activity, exhibited by enzymes vanadate-dependent haloperoxidases, has been considered as one of the important catalytic reactions [1–3]. Several vanadium and molybdenum complexes model this reaction [4,5]. Vanadium complexes also present functional model of haloperoxidases where these complexes catalyze the oxidative halogenation of aromatic substrates using H₂O₂ as oxidant in the presence of halides [3,6,7]. They have also been shown to be active homogeneous catalysts for

other oxidation reactions [8,9]. Oxovanadium(IV) complexes encapsulated in the cavity of zeolite-Y have also been reported and studied for the oxidation reactions. For example oxovanadium(IV) complexes of H₂salen-based ligands encapsulated in zeolite-Y have shown good catalytic activity for the oxidation of phenol [10–12]. Complex, [VO(pic)₂] encapsulated in zeolite-Y has been studied for the oxidation of cyclohexene, *n*-hexane and toluene [13]. Leaching of the catalysts encapsulated in zeolite-Y has, however, been observed during catalytic action if the molecular size of the catalysts are too small [14]. Similarly copper(II) complexes encapsulated in the cavity of zeolite-Y exhibit several oxidation reactions [15,16].

In this paper, encapsulation of oxovanadium(IV) and copper(II) complexes of 2-mercaptomethylbenzimidazole (Htmbmz, **I**; Scheme 1), their characterization and catalytic

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I: Htmbmz

Scheme 1.

activities for the oxidation of styrene, methyl phenyl sulfide and diphenyl sulfide are reported.

2. Experimental

2.1. Materials and methods

Mercapto acetic acid (E. Merck, India), methyl phenyl sulfide (Alfa Aesar, USA) and diphenyl sulfide (Himedia, India) were used as obtained. Y-zeolite (Si/Al ~ 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were of AR grade.

2.2. Physical methods and analysis

Inductively coupled plasma spectrometer (ICP; Labtam 8440 plasmalab) were used for copper and vanadium estimation after leaching the metal ions with concentrated nitric acid and diluting with distilled water (for copper) or with very dilute aqueous KOH solution (for vanadium) to specific volume in volumetric flask. Thermogravimetric analyses of 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 α target. IR spectra were recorded as KBr pellet on a Nicolet NEXUS Aligent 1100 series FT-IR spectrometer after grinding the sample with KBr. 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. All catalyzed reaction products were analyzed using Thermoelectron gas-chromatograph having HP-1 capillary column (30 m \times 0.25 mm \times 0.25 μ m) and FID detector. The identities of the products were confirmed by GC–MS model Perkin-Elmer, Clarus 500.

2.3. Preparations

2.3.1. Preparation of 2-mercaptomethylbenzimidazole (Htmbmz, I)

A mixture of *o*-phenylenediamine (10.8 g, 100 mmol) and mercaptoacetic acid (9.1 g, 100 mmol) was dissolved in 4 M HCl (150 ml) and the reaction mixture was refluxed for 24 h on a heating mantle. After keeping the flask at 10 °C overnight, the precipitated greenish crystals of Htmbmz·HCl were filtered off and washed with acetone. On neutralization of Htmbmz·HCl dissolved in minimum of water with K₂CO₃, yellow green

solid of Htmbmz separated out which was filtered, washed with minimum amount of cold water and dried in desiccator over NaOH. Yield: 68%. Anal. found: C, 58.49%; H, 4.77%; N, 17.26%; S, 19.72%. Calcd. for C₈H₁₄N₂S (164.0): C, 58.53%; H, 4.88%; N, 17.07%; S, 19.51%. mp: 157 °C (Lit. 157–158 °C) [17].

2.3.2. Preparation of M-Y (M = Cu(II) or OV(IV))

An amount of 5.0 g of Na-Y zeolite was suspended in 300 ml of distilled water and to this was added cupric nitrate (2.8 g, 12 mmol) for Cu(II)-Y or vanadyl sulfate (3.0 g, 12 mmol) for OV(IV)-Y with stirring at ca. 90 °C for 24 h. The light color solid was filtered off, washed with hot distilled water until filtrate was free from any metal ion content and dried at ca. 120 °C for 24 h.

2.3.3. Preparation of [VO^{IV}(tmbmz)₂]-Y (1) and [Cu^{II}(tmbmz)₂]-Y (2)—a general method

Encapsulated complexes were prepared using flexible ligand method. An amount of 1.0 g of Cu(II)-Y or OV(IV)-Y and 2.5 g ligand were mixed in 50 ml of methanol in a round bottom flask and the reaction mixture was heated under reflux for overnight in an oil bath while stirring. The resulting material was filtered, dried and soxhlet extracted with methanol followed by acetone to remove excess ligand and metal complex on the surface of zeolite. The uncomplexed metal ions in zeolite were removed by treating with aqueous 0.01 M NaCl solution (200 ml) with stirring for 8 h. It was then washed with double distilled water till no precipitate of AgCl was observed in the filtrate on treating with AgNO₃. Finally they were dried at 120 °C till constant weight.

2.3.4. Preparation of [VO^{IV}(tmbmz)₂] (3)

A solution of VOSO₄·5H₂O (1.25 g, 5 mmol) in minimum amount of water was added drop wise to a methanolic solution of Htmbmz (1.63 g, 10 mmol) and the obtained reaction mixture was refluxed on a water bath for 2 h. After keeping the flask at ambient temperature for over night, complex [VO(tmbmz)₂] slowly separated out, which was filtered, washed with methanol and dried in vacuum over silica gel. Yield: 65%. Anal. found: C, 48.71%; H, 3.65%; N, 14.12%; S, 16.10%; V, 12.55%. Calcd. for C₁₆H₁₄N₄S₂VO (393.38): C, 48.85%; H, 3.59%; N, 14.24%; S, 16.30%; V, 12.95%.

2.3.5. Preparation of [Cu^{II}(tmbmz)₂] (4)

A solution of Cu(CH₃COO)₂·H₂O (1.0 g, 5 mmol) dissolved in 50 ml of methanol was added to a methanolic solution of Htmbmz (1.63 g, 10 mmol) with stirring. After addition of KOH (0.28 g, 5 mmol) dissolved in 5 ml of water with stirring, the reaction mixture was further stirred for 2 h. During this period [VO(tmbmz)₂] slowly separated out, which was filtered off, washed with minimum amount of methanol and dried in vacuum over silica gel. Yield: 70%. Anal. found: C, 48.90%; H, 3.94%; N, 13.96%; S, 16.30%; Cu, 15.62%. Calcd. for C₁₆H₁₄N₄S₂Cu (389.99): C, 49.28%; H, 3.62%; N, 14.37%; S, 16.44%; Cu, 16.29%.

2.4. Catalytic activity studies

2.4.1. Oxidation of styrene

The catalytic oxidation of styrene was carried out using complexes, $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ in a 50 ml flask fitted with a water circulated condenser. In a typical reaction, an aqueous solution of 30% H_2O_2 (2.27 g, 20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH_3CN and the reaction mixture was heated at 80°C with continuous stirring in an oil bath. The reaction was considered to begin after addition of 0.025 g of catalyst. During the reaction, the products were analyzed using a gas chromatograph by withdrawing small aliquots after specific interval of time and confirming their identities by GC–MS.

2.4.2. Oxidation of methyl phenyl sulfide and diphenyl sulfide

The catalytic oxidation of methyl phenyl sulfide and diphenyl sulfide was carried out using $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ in a 50 ml flask at room temperature. Methyl phenyl sulfide (0.62 g, 0.005 mmol) or diphenyl sulfide (0.93 g, 5 mmol) and 30% H_2O_2 (0.57 g, 5 mmol) was dissolved in 20 ml of acetonitrile. After addition of catalyst (0.015 g), the reaction mixture was stirred at room temperature for 3 h or 7 h, respectively for methyl phenyl sulfide or diphenyl sulfide. During this period, the reaction products formed were analyzed using gas chromatograph by withdrawing small aliquots after specific interval of time. The identities of the products were confirmed by GC–MS.

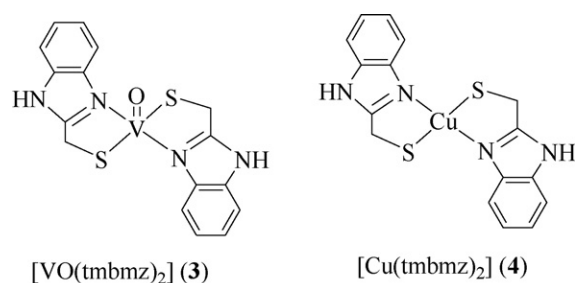
3. Results and discussion

3.1. Characterization of catalysts

Syntheses of zeolite-Y encapsulated complexes represented as $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (1) and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ (2) were completed in two steps. The first step involved the exchange of oxovanadium(IV) and copper(II) ions with Na^+ of Na-Y while second step involved the reaction of metal exchanged zeolite-Y with Htmbmz (I) in methanol. Here, ligand entered into the cavity of zeolite-Y due to its flexible nature and interacted with metal ions. The crude mass was extracted with methanol and acetone to remove excess free ligand and neat metal complex formed on the surface of the zeolite, if any. The percentages of metal content determined before and after encapsulation by inductively coupled plasma along with their expected formula and color are presented in Table 1. As crude mass was extracted with methanol and acetone the metal ion content found after encapsulation is only due to the presence of metal complexes in the nano-cavity of

Table 1
Chemical composition, physical and analytical data

No.	Catalyst	Color	Metal content (wt%)
1	OV(IV)-Y	Light green	4.58
2	Cu(II)-Y	Pale blue-green	7.60
3	$[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (1)	Light green	1.14
4	$[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ (2)	Yellow green	2.58



Scheme 2. Proposed structures for neat complexes.

the zeolite-Y. The molecular formula of the complexes are based on the neat complexes $[\text{VO}(\text{tmbmz})_2]$ and $[\text{Cu}(\text{tmbmz})_2]$ that have also been prepared by reacting the corresponding suitable metal precursor with the ligand and characterized.

Based on various studies, the following structures (Scheme 2) have been proposed for the complexes; encapsulated complexes are expected to have similar structures. Structures of these complexes can be compared directly with the copper(II) and oxovanadium(IV) complexes of 2-(α -hydroxyalkyl)benzimidazole [18,19]. The reported complexes will fit nicely in the cavity of the zeolite-Y and the size of the complexes will be larger than the window size of zeolite-Y because of the presence of two bulky benzimidazole groups from two ligands in each complex. It should be noted that in $[\text{Cu}(\text{salen})]$ complex where only two salicylaldehyde moieties are present, has diagonal distance of ca. 10 \AA . Thus, the diagonal distances of $[\text{Cu}(\text{tmbmz})_2]$ and $[\text{VO}(\text{tmbmz})_2]$ will be approximately of same size. No leaching or escaping of complexes (vide infra) has been observed during catalytic action of complexes in solvent, which further supports the above statement.

3.2. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na-Y, OV(IV)-Y and Cu(II)-Y, and encapsulated metal complexes were recorded at 2θ values between 5° and 50° . The XRD patterns of Na-Y, Cu(II)-Y and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ are presented in Fig. 1. An

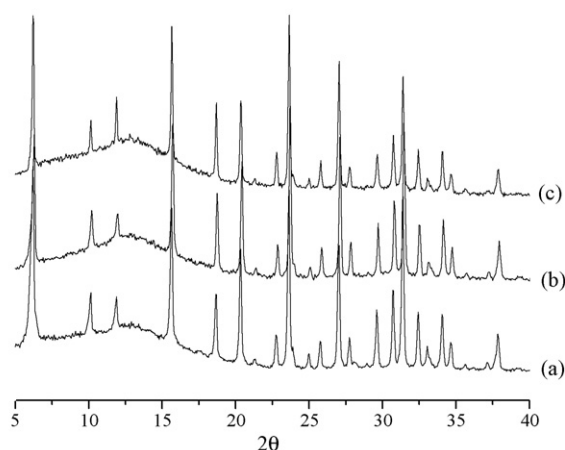


Fig. 1. XRD patterns of Na-Y (a), Cu-Y (b) and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ (c).

Table 2
Thermogravimetric analysis data of catalysts

Catalyst	Temperature range (°C)	Weight loss (%)	Group lost
[VO(tmbmz) ₂]-Y	70–150	4.5	H ₂ O
	150–280	5.8	nH ₂ O
	280–800	13.0	tmbmz
[Cu(tmbmz) ₂]-Y	70–150	5.1	H ₂ O
	150–280	5.2	nH ₂ O
	280–800	13.4	tmbmz

essentially similar pattern in Na-Y, metal ions exchanged zeolite and encapsulated metal complexes were noticed, though slight change in the intensity of the bands in encapsulated complexes is in line. These observations indicate that the framework of the zeolite has not undergone any significant structural change during incorporation of the catalysts, i.e. crystallinity of the zeolite-Y is preserved during encapsulation. No new peaks due to neat complex were detected in the encapsulated zeolite possibly due to very low percentage loading of metal complexes.

3.3. Thermogravimetric analysis

The thermogravimetric analysis data along with the percent weight loss at different steps and their possible assignments are presented in Table 2. TG and DTG profile of one representative complex [Cu(tmbmz)₂]-Y is reproduced in Fig. 2. The thermal decomposition of catalysts [VO(tmbmz)₂]-Y (**1**) and [Cu(tmbmz)₂]-Y (**2**) usually occurs in three steps. The removal of just trapped water of ca. 4.5% (in **1**) or ca. 5.1% (in **2**) occurs up to 150 °C, while an endothermic weight loss of ca. 5.8% (in **1**) or ca. 5.2% (in **2**) associated with removal of intrazeolite water occurs in the temperature range of 150–280 °C. The third step of exothermic weight loss consists of several sub-steps and starts immediately after second step and continues till 800 °C to constant weight. A weight loss of ca. 13.0% (in **1**) or ca. 13.4% (in **2**) due to the slow decomposition of metal complexes is expected in this wide temperature range. The loss in percentage is in agreement with the percentage of metal content obtained for encapsulated complexes.

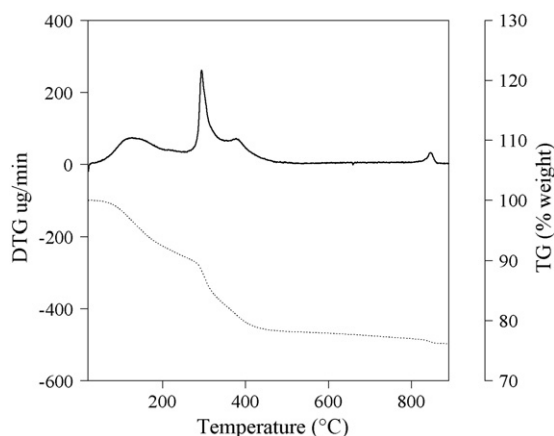


Fig. 2. TG (dotted line) and DTG (solid line) profile of [Cu(tmbmz)₂]-Y.

Table 3
IR and electronic spectral data of ligand, pure and encapsulated complexes

Compound	IR (cm ⁻¹)		λ_{\max} (nm) ^a
	$\nu(\text{C}=\text{N})$	$\nu(\text{V}=\text{O})$	
Htmbmz	1638		205, 252, 278, 284, 327(s)
[VO(tmbmz) ₂]-Y	1632	–	206, 275, 388
[Cu(tmbmz) ₂]-Y	1627		203, 312, 388
[VO(tmbmz) ₂]	1628	979	210, 240, 274, 280, 289(s), 396(s), 524, 665
[Cu(tmbmz) ₂]	1626		209, 230, 274, 280, 297, 382

^a s indicates shoulder band.

3.4. IR spectral studies

A partial list of IR spectral data of ligand, neat as well as encapsulated complexes are presented in Table 3. The intensity of the peaks in encapsulated complexes is, though, weak due to their low concentration in zeolite matrix, the spectra of encapsulated as well as neat complexes show 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 Htmbmz exhibits a sharp band at 1638 cm⁻¹ due to $\nu(\text{C}=\text{N})$ (azomethine) and this band shifts to lower wave number on coordination of azomethine nitrogen to the metal ion and appears at 1626–1632 cm⁻¹. The $\nu(\text{C}-\text{S})$ (thioalcoholic) of ligand appears at 747 cm⁻¹ and this band shift towards lower wave number thereby indicating the coordination of sulfur to the vanadium [20]. Neat complex [VO(tmbmz)₂] exhibits a sharp band at 979 cm⁻¹ due to $\nu(\text{V}=\text{O})$ stretch, while the location of such $\nu(\text{V}=\text{O})$ band in zeolite encapsulated vanadium complex was not possible due to the appearance of a strong and broad band at ca. 1000 cm⁻¹ due to zeolite frame work.

3.5. Electronic spectral studies

Electronic spectrum of ligand Htmbmz in methanol exhibits five bands at 205, 252, 278, 284 and 327 nm (Table 5). The band at 278 and 284 nm are characteristics of the presence of benzimidazole group [21]. Other three bands are assignable to $\phi-\phi^*$, $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively. In the electronic spectrum of neat complex, [Cu(tmbmz)₂], the characteristic bands appear at 274 and 280 nm while other ligand bands appear at 229, 236 and 297 nm. A medium intensity band appearing at 382 nm is assigned to ligand to metal charge transfer band. Vanadium complex, [VO(tmbmz)₂] also exhibits characteristic bands at 274 and 280 nm along with other ligand bands. The weak shoulder band appearing at 396 nm is assignable to ligand to metal charge transfer band. In addition, two weak shoulder bands at 524 and 665 nm in [VO(tmbmz)₂] at higher concentration have also been observed and are considered due to d–d transitions. Such band in copper(II) complex could not be located. Both the encapsulated complexes exhibit essentially similar spectral patterns with bands at 206, 275 and 388 nm in vanadium and 203, 312, 388 nm in copper complex (Fig. 3). Presence of these bands confirms the existence of complexes in the cavity of zeolite-Y.

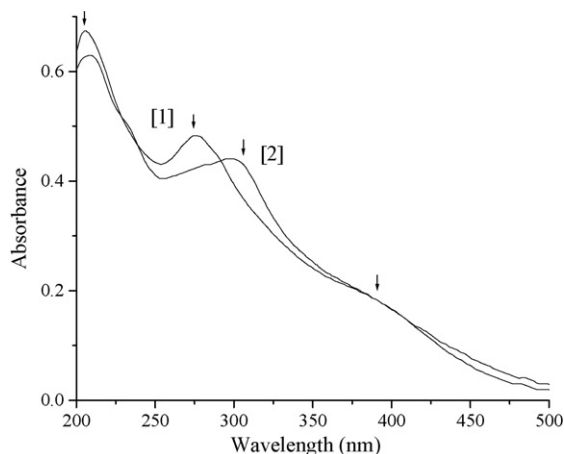


Fig. 3. Electronic spectra of $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (1) and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ (2).

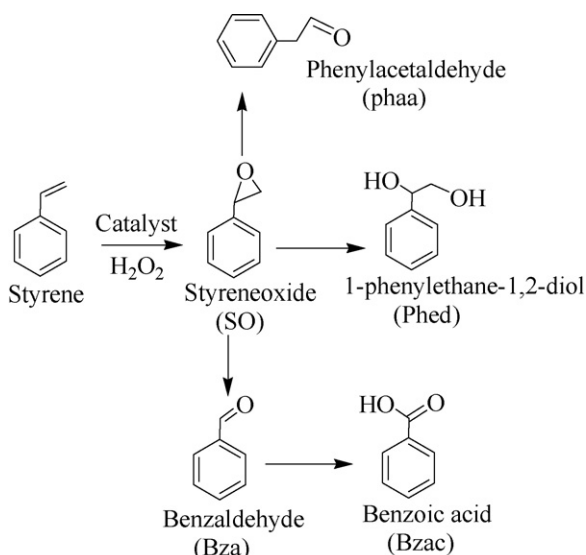
3.6. Catalytic activity studies

3.6.1. Oxidation of styrene

The oxidation of styrene was carried out by H_2O_2 using $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ as catalysts and five oxidation products, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenyl acetaldehyde along with only minor amounts of unidentified products were obtained. Scheme 3 represents the formation of all these products. These products have also been identified earlier [22–24].

In search of suitable reaction conditions to achieve the maximum oxidation of styrene catalyzed by these catalysts, the effect of three different reaction parameters, viz. amount of oxidant and catalyst, and temperature of the reaction mixture have been studied in details using $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ as a representative catalyst.

The effect of H_2O_2 concentration on the oxidation of styrene is illustrated in Fig. 4. Four different H_2O_2 /styrene molar ratios of 1:1, 2:1, 3:1 and 4:1 were considered, while keeping the other parameters fixed as styrene (1.04 g, 10 mmol) and catalyst



Scheme 3.

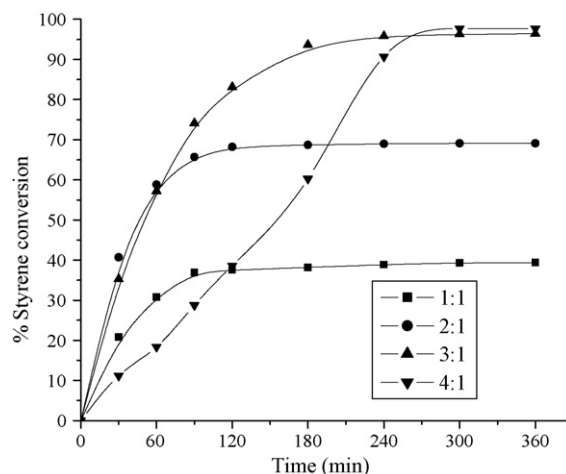


Fig. 4. Effect of H_2O_2 concentration (H_2O_2 :styrene) on the oxidation of styrene.

$[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (0.035 g) in 20 ml of CH_3CN and the reaction was carried out at 80°C . Increasing the H_2O_2 /styrene ratio increases the conversion from 39.4% for 1:1 to 69.1% for 2:1 and finally to 96.4% for 3:1 molar ratio in 6 h of reaction time. No further increase in conversion was obtained beyond this molar ratio. The oxidant to substrate mole ratio of 3:1 was, therefore, considered for optimizing the other reaction conditions. For the optimization of the amount of catalyst, five different amounts of catalyst, viz. 0.015, 0.025, 0.035, 0.050 and 0.075 g were considered while keeping a fixed amount of styrene (1.04 g, 10 mmol) and H_2O_2 (3.42 g, 30 mmol) in 20 ml of CH_3CN and the reaction was carried out at 80°C . As illustrated in Fig. 5, the conversion increases on increasing the amount of catalyst and reached to a maximum of 96.4% with 0.035 g of catalyst while either more or less molar ratio gave lower conversions. The reason for fewer activities at higher catalyst dose may possibly be due to adsorption/chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact. Therefore, an amount of 0.035 g catalyst may be considered as appropriate to obtain the maximum conversion of styrene. Fig. 6 illustrates the effect of oxidation of styrene at different temperatures and as

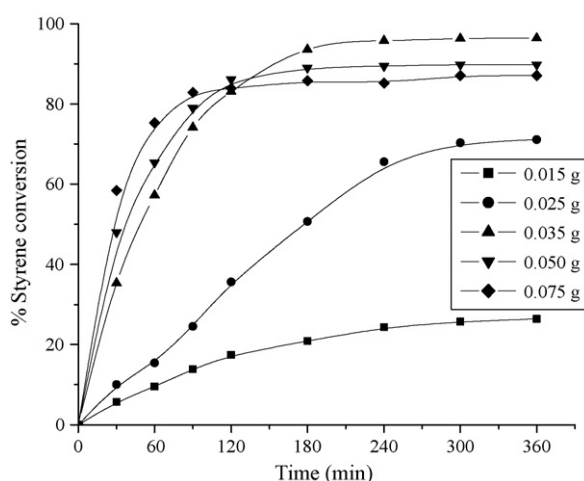


Fig. 5. Effect of amount of catalyst on the oxidation of styrene.

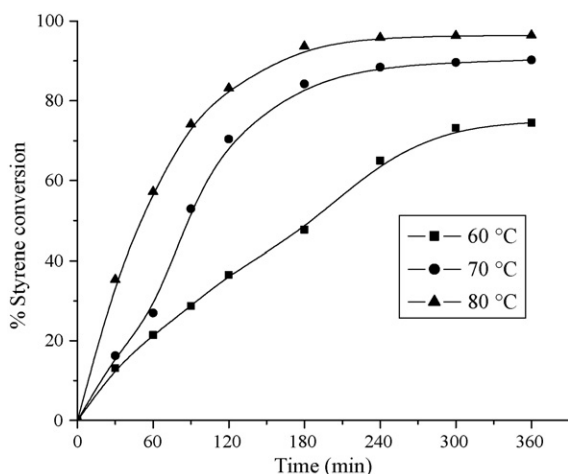


Fig. 6. Effect of temperature on the oxidation of styrene.

observed earlier, running the reaction at 80 °C while keeping the other conditions optimized as above gave a highest conversion of 96.4% in 6 h of reaction time. Thus, for the maximum oxidation of 10 mmol of styrene other required reagents were: [VO(tmbmz)₂]-Y (0.035 g), H₂O₂ (3.42 g, 30 mmol), CH₃CN (20 ml) and temperature (80 °C).

After acquiring the optimized reaction conditions for [VO(tmbmz)₂]-Y, catalyst [Cu(tmbmz)₂]-Y was also tested using same reaction conditions. Fig. 7 compares the efficiency of both catalysts as a function of time while Table 4 provides conversion percentage of styrene and selectivity details of various products. It is clear from the table that the performance of [Cu(tmbmz)₂]-Y is much poorer in comparison to that of [VO(tmbmz)₂]-Y and only four products namely, styrene oxide, benzaldehyde, benzoic acid and phenylacetaldehyde are identified as a result of oxidation. Amongst the different products formed by the two catalysts, the selectivity of styrene oxide is better for [Cu(tmbmz)₂]-Y (12.9%) than [VO(tmbmz)₂]-Y (6.1%), while both catalysts gave benzaldehyde in highest yield. The yields of other products are much smaller and are comparable. Blank reaction under above-optimized reaction conditions exhibited only 3% conversion. The mechanism for the oxidation of styrene and the formation of oxidation products have been discussed earlier in details [23,25].

Neat complexes, [VO(tmbmz)₂] and [Cu(tmbmz)₂] were also tested for the oxidation of styrene using same mole concentration of complex as in their respective zeolite encapsulated

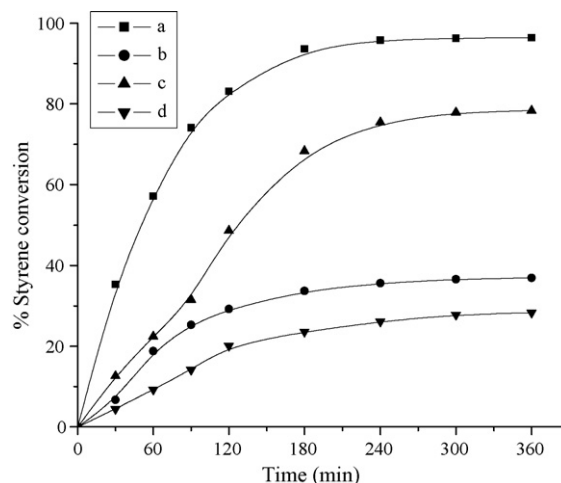


Fig. 7. Catalytic comparison of catalysts for the oxidation of styrene with H₂O₂ as oxidant: [VO(tmbmz)₂]-Y (a), [Cu(tmbmz)₂]-Y (b) and [VO(tmbmz)₂] (c) and [Cu(tmbmz)₂] (d).

Table 5

Products selectivity and percent conversion of styrene with TBHP as oxidant after 6 h of reaction time

Catalyst	% Conversion	TOF (h ⁻¹)	% Product selectivity		
			so	bza	Other
[VO(tmbmz) ₂]-Y	22.4	47.7	55.5	38.6	5.9
[Cu(tmbmz) ₂]-Y	48.2	56.6	57.7	38.2	4.1
[VO(tmbmz) ₂]	13.6	28.9	52.6	42.7	4.7
[Cu(tmbmz) ₂]	34.7	40.7	53.3	41.1	5.6

ones under above reaction conditions. The conversion details are also presented in Fig. 7 and Table 4. Neat complexes exhibited lower conversions than their encapsulated analogues. However, the formation of the products and their activity order are same as obtained by respective encapsulated complexes.

Under the above-optimized reaction conditions, catalytic action of [VO(tmbmz)₂]-Y and [Cu(tmbmz)₂]-Y along with their neat analogues were also tested using TBHP as an oxidant, i.e. 30 mmol 70% TBHP and 0.035 g catalyst for 10 mmol styrene were taken in 20 ml of CH₃CN and reaction was carried out at 80 °C. Neat complexes have also been tested using same mole concentrations as taken for respective encapsulated complexes. Fig. 8 provides the percentage conversion as a function of time and Table 5 compares the selectivity

Table 4

Products selectivity and percent conversion of styrene with H₂O₂ as oxidant after 6 h of reaction time

Catalyst	% Conversion	TOF (h ⁻¹) ^a	% Product selectivity ^b					
			so	bza	phed	bzac	phaa	Other
[VO(tmbmz) ₂]-Y	96.4	205.4	6.1	68.1	12.4	9.6	2.3	1.5
[Cu(tmbmz) ₂]-Y	36.9	43.3	12.9	74.8	–	8.2	2.9	1.2
[VO(tmbmz) ₂]	78.3	166.8	5.4	70.6	11.5	8.3	2.6	1.6
[Cu(tmbmz) ₂]	28.3	33.2	10.7	73.2	–	10.6	3.4	2.1

^a TOF (h⁻¹) (turn over frequency): moles of substrate converted per mole of metal ion (in the solid state catalyst) per hour.

^b so, styrene oxide; baz, benzaldehyde; phed, 1-phenylethane-1,2-dione; bzac, benzoic acid; phaa, phenylacetaldehyde.

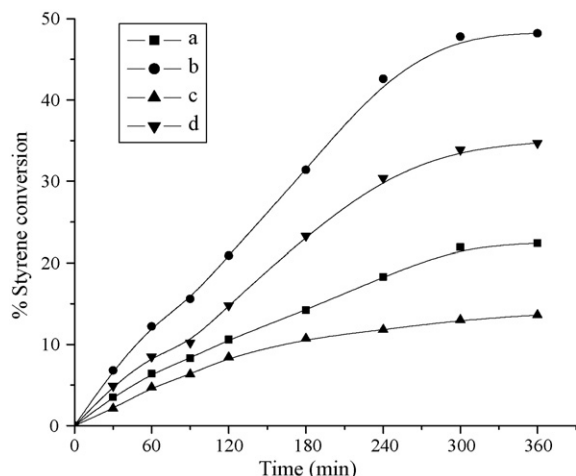


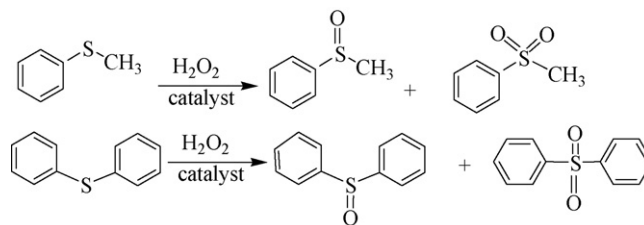
Fig. 8. Catalytic comparison of catalysts for the oxidation of styrene with TBHP as oxidant: $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (a), $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ (b), $[\text{VO}(\text{tmbmz})_2]$ (c) and $[\text{Cu}(\text{tmbmz})_2]$ (d).

data along with the conversion percentage and turn over frequency (TOF) after 6 h of reaction time. It is clear that under the optimized conditions, the obtained percentage conversion varied in the order: $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ (48.2%) > $[\text{Cu}(\text{tmbmz})_2]$ (34.7%) > $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (22.4%) > $[\text{VO}(\text{tmbmz})_2]$ (13.6%). Thus, the conversion of styrene with all these catalysts are relatively low but the selectivity of the formation of styrene oxide is considerably high (52.6–57.7%) whereas, the selectivity of benzaldehyde is low (38.2–42.7%). Only small amount of the formation of other products is possibly due to no further oxidation of styrene oxide to other oxidized products as observed above due to the mild oxidizing nature of TBHP.

Catalytic potential of these complexes compare well with similar encapsulated complexes. The observed conversions for zeolite-Y encapsulated complexes $[\text{Mn}(\text{Cl}_2\text{-haacac})\text{Cl}]\text{-NaY}$ (89.7%) [26], $[\text{Mn}(\text{NO}_2)_2\text{-haacac}]\text{Cl}\text{-NaY}$ (96.9%) (H_2haacac = bis(2-hydroxyanyl)acetylacetonone) [27] with *tert*-butylhydroperoxide as initiator and air as oxidant are close to the one reported in Table 4. Zeolite encapsulated catalysts $[\text{Mn}(3\text{-MeOsalen})]\text{-Y}$ (H_2salen = bis(salicylaldehyde)-1,2-diaminoethane), $[\text{Mn}(3\text{-MeOsaln})]\text{-Y}$, $[\text{Mn}(\text{salpn})]\text{-Y}$ (H_2salpn = bis(salicylaldehyde)-1,3-diaminopropane) and $[\text{VO}(\text{salphen})]$ ($\text{H}_2\text{salphen}$ = Schiff base derived from salicylaldehyde and *o*-phenylenediamine) exhibit 17%, 8.7%, 7.4% [28] and 34.8% [22] conversions, respectively, using *tert*-butylhydroperoxide as oxidant. Zeolite-Y encapsulated catalyst $[\text{VO}_2(\text{sal-ambmz})]\text{-Y}$ and $[\text{Cu}(\text{sal-ambmz})\text{Cl}]\text{-Y}$ (Hsal-ambmz = Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole) exhibits ca. 97 and 56.7% conversion of styrene, respectively, using H_2O_2 as an oxidant [25].

3.6.2. Oxidation of methyl phenyl sulfide and diphenyl sulfide

The sulfur atom of the diphenyl sulfide and methyl phenyl sulfide is electron rich and has been shown to undergo electrophilic oxidation to give sulfoxide. Such oxidation of methyl phenyl sulfide and diphenyl sulfide by aqueous 30% H_2O_2 has



Scheme 4.

been carried out using $[\text{VO}_2(\text{tmbmz})_2]\text{-Y}$ and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ as catalyst. Scheme 4 presents the oxidation products of both sulfides.

Again, reaction conditions have been optimized for the maximum oxidation of diphenyl sulfide considering $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ as a representative catalyst and two different parameters, viz. amounts of oxidant and catalyst were varied.

The effect of H_2O_2 concentration on the oxidation of diphenyl sulfide is illustrated in Fig. 9. Using three different concentrations of aqueous 30% H_2O_2 , viz. 5 mmol (0.057 g), 10 mmol (1.14 g) and 15 mmol (1.71 g) for the fixed amount of diphenyl sulfide (0.93 g, 5 mmol) and $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ (0.025 g) in CH_3CN (10 ml), the obtained percent conversion of diphenyl sulfide were 24.6, 70.6 and 91.7%, respectively, in 7 h of reaction time at room temperature. No further improvement in the conversion was noted above this molar ratio. Similarly for four different amounts (viz. 0.005, 0.015, 0.025 and 0.035 g) of catalyst and at H_2O_2 to diphenyl sulfide molar ratio of 3:1 under above reaction conditions, 0.025 g of catalyst gave a conversion of 91.7% while 0.035 g catalyst has shown only slight improvement in the conversion (Fig. 10). Thus, 0.025 g catalyst may be considered sufficient enough to run the reaction under above conditions.

While carrying out the oxidation of methyl phenyl sulfide under above-optimized conditions, it was observed that the substrate to H_2O_2 molar ratio of 1:1, was sufficient enough to give 94.3% conversion within 3 h of contact time. Increasing the

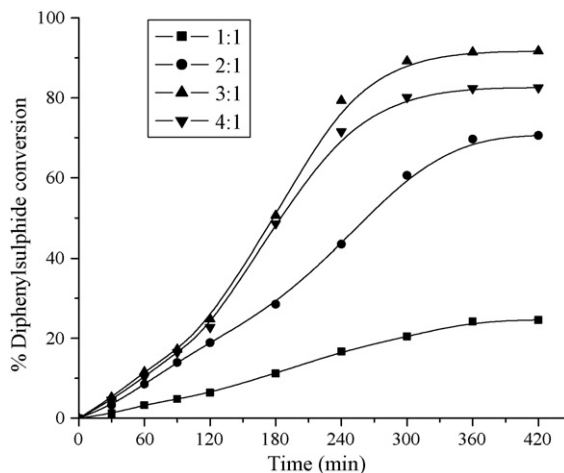


Fig. 9. Effect of H_2O_2 concentration (H_2O_2 :diphenyl sulfide) on the oxidation of diphenyl sulfide.

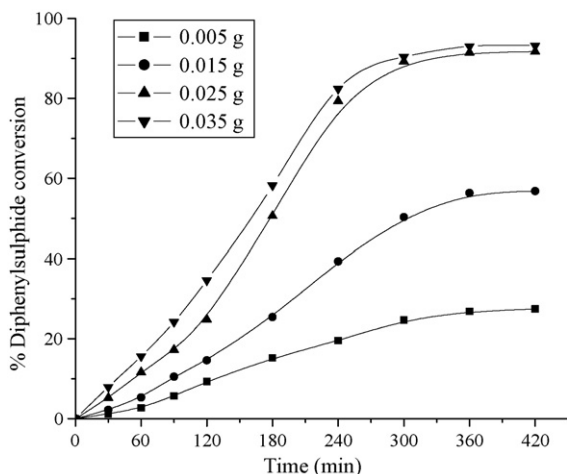


Fig. 10. Effect of catalyst amount on the oxidation of diphenyl sulfides.

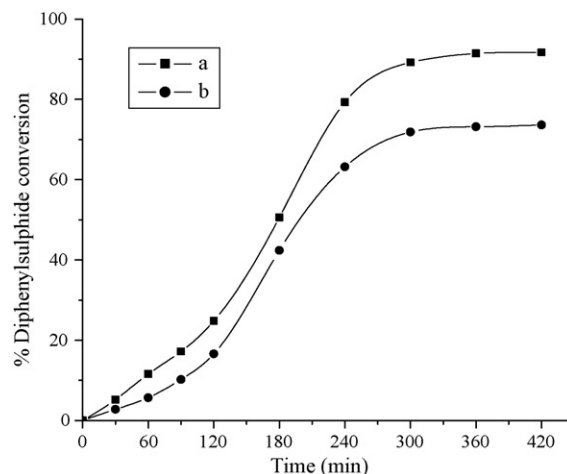


Fig. 11. Catalytic comparison of catalysts for the oxidation of diphenyl sulfide: [VO(tmbmz)₂]-Y (a) and [VO(tmbmz)₂] (b).

amount of oxidant to 2:1 (oxidant:substrate) molar ratio caused only marginal increment in the conversion. Thus, the substitution of benzene in place of methyl group slows down the conversion. Selectivity details for the obtained products are presented in Table 6. It is clear from the table that catalyst [VO(tmbmz)₂]-Y has good catalytic potential for both substrates with high turn over frequency. But the selectivity for the formation of methyl phenyl sulfoxide is better (88.9%) than for diphenyl sulfoxide (72.9%). A blank reaction taking methyl phenyl sulfide (1.242 g, 10 mmol), aqueous 30% H₂O₂ (2.27 g, 20 mmol) and acetonitrile (10 ml) resulted in 35.2% conversion with 68.3% selectivity towards sulfoxide and 31.7% sulfone. Blank reaction for diphenyl sulfide under above reaction conditions gave only 5.5% conversion with 66% selectivity towards sulfide and 34% towards sulfone. Thus, these catalysts not only improve conversion, they also improve the selectivity of the formation of sulfoxide.

The catalytic activity of neat complexes using same mole concentration as used for encapsulated complexes under above reaction conditions have also been tested for comparison. Fig. 11 compares the conversion of diphenyl sulfide with neat as well as encapsulated complexes while Fig. 12 compares the conversion of methyl phenyl sulfide. As presented in Table 6, neat complex exhibited relatively lower conversion to that of encapsulated one. The uniform dispersal of active metal centers in the zeolite matrix prevents the loss of catalytic activity thus showing better catalytic results.

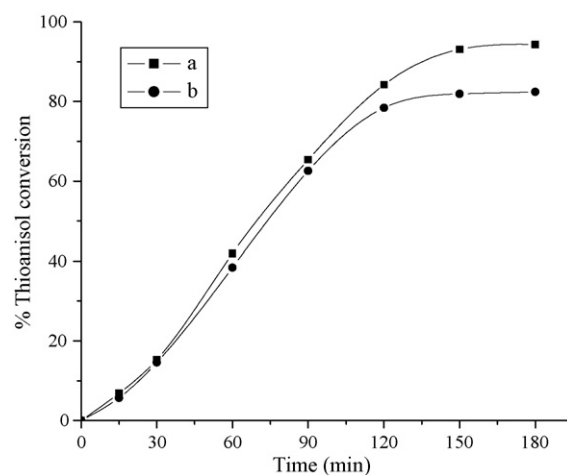


Fig. 12. Catalytic comparison of catalysts for the oxidation of thioanisol: [VO(tmbmz)₂]-Y (a) and [VO(tmbmz)₂] (b).

Table 6
Percent conversion of sulfides along with TOF and products selectivity data

Catalyst	Substrate	% Conversion/time (h)	TOF (h ⁻¹)	% Selectivity	
				Sulfoxide	Sulfone
[VO(tmbmz) ₂]-Y	Diphenyl sulfide	91.7/7	117.2	72.9	27.1
[VO(tmbmz) ₂]-Y	Methyl phenyl sulfide	94.3/3	281.2	88.9	11.1
[VO(tmbmz) ₂]	Diphenyl sulfide	73.6/7	94.1	77.8	22.2
[VO(tmbmz) ₂]	Methyl phenyl sulfide	82.4/3	245.7	90.3	9.7

3.7. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the neat complexes dissolved in methanol were treated with methanolic solution of H₂O₂ and the progress of the reaction was monitored by electronic absorption spectroscopy. Thus, the titration of [VO(tmbmz)₂] dissolved in methanol (ca. 10⁻⁴ M solution) with one drop portions of 30% H₂O₂ resulted in the slow weakening of 240 nm band with decrease in intensity while 210 nm band experienced slight increase in intensity. The band appear-

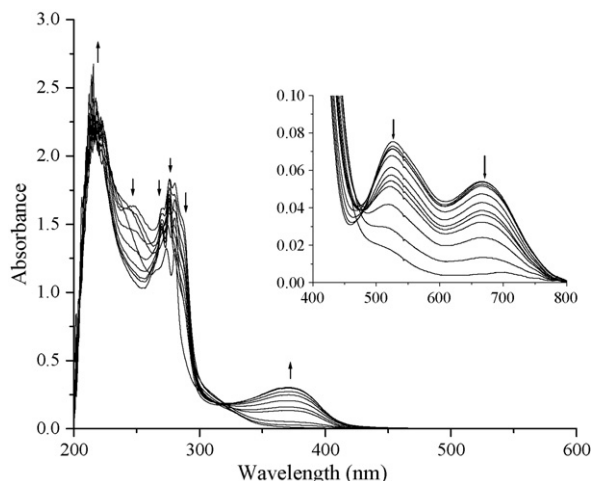


Fig. 13. Spectral changes during titration of $[\text{VO}(\text{tmbmz})_2]$ with H_2O_2 . The spectra were recorded after successive addition of one drop portions of H_2O_2 in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of $[\text{VO}(\text{tmbmz})_2]$ in methanol. The inset displays equivalent titrations, but with higher concentration of $[\text{VO}(\text{tmbmz})_2]$ (ca. 10^{-3} M) dissolved in methanol.

ing at 274, 280 and 289(s) nm experienced slight decrease in intensity. At the same time the weak shoulder band appearing at 396 nm shifted to 370 nm with increase in intensity. The band appearing at 524 and 665 nm due to d–d transitions at higher concentration of $[\text{VO}(\text{tmbmz})_2]$ (ca. 10^{-3} M) slowly disappeared on addition of H_2O_2 . These spectral changes and the presence of isosbestic point at 325 nm suggest the interaction of oxovanadium(IV) complex with H_2O_2 possibly to give oxoperovanadium(V) species. The spectral changes are presented in Fig. 13.

As shown in Fig. 14, the addition of one drop portions of 30% H_2O_2 dissolved in methanol to a methanolic solution of $[\text{Cu}(\text{tmbmz})_2]$ (ca. 10^{-4} M solution) resulted in the gradual increment of the intensity of bands appearing at 274 and 280 nm.

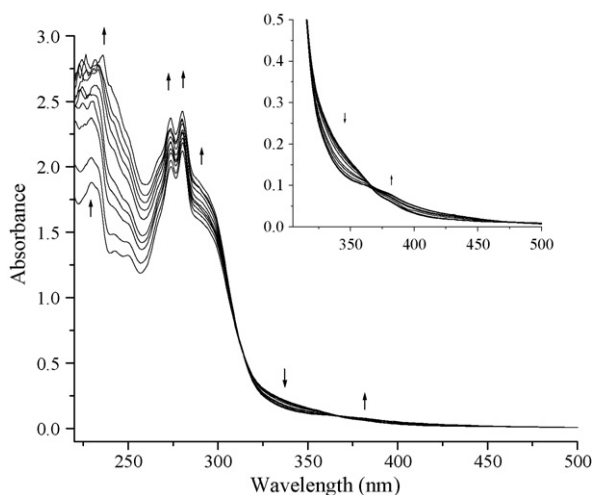


Fig. 14. Spectral changes during titration of $[\text{Cu}(\text{tmbmz})_2]$ with H_2O_2 . The spectra were recorded after successive addition of one drop portions of H_2O_2 in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of $[\text{Cu}(\text{tmbmz})_2]$ in methanol. The inset displays equivalent titrations, but with higher concentration of $[\text{Cu}(\text{tmbmz})_2]$ (ca. 10^{-3} M) dissolved in methanol.

Other band appearing at 230 nm shifts slowly to 236 nm with increase in band maximum while the band at 297 nm slowly broadens with slight increase in intensity. A very weak shoulder band appearing at 382 nm slowly disappears (see inset of Fig. 14). No other bands could be located in the visible region beyond this point. It was, therefore, not possible to have idea about the change in the d–d transition band(s) due to H_2O_2 titration. However, the spectral changes in the UV region on treatment with H_2O_2 suggest the structural changes due to the formation of intermediate peroxy species, which finally transfers oxygen to the organic substrates.

3.8. Test for recycle ability and heterogeneity of the reactions

The recycle ability of both the encapsulated complexes has been tested. For styrene, the reaction mixture after a contact time of 6 h was filtered and after activating the catalysts by washing with acetonitrile and drying at ca. 120°C , they were subjected to further catalytic reaction under similar conditions. No appreciable loss in the catalytic activity suggests that complexes are still present in the cavity of the zeolite-Y. Nearly matching spectral features (IR and electronic spectra) of fresh and used catalysts suggests their stability and recycle ability. The filtrate collected after separating the used catalysts 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. Similar results were also obtained with other substrates. All these confirm that the reactions did not proceed upon removal of the solid catalysts. The reactions were, therefore, heterogeneous in nature.

4. Conclusions

Encapsulation of oxovanadium(IV) and copper(II) complexes of monobasic bidentate NS donor ligand, 2-mercaptomethylbenzimidazole (Htmbmz) in the cavity of zeolite-Y by flexible ligand method have been described. These complexes have been characterized by various physico-chemical methods. The encapsulated complexes, $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ and $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ have been used as catalysts for the oxidation of styrene, methyl phenyl sulfide and diphenyl sulfide. Under the optimized reaction conditions, $[\text{VO}(\text{tmbmz})_2]\text{-Y}$ gave 96.4% conversion of styrene with five oxidation products, styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde. Conversion with $[\text{Cu}(\text{tmbmz})_2]\text{-Y}$ is considerably low (36.9%) and gave only four products, styrene oxide, benzaldehyde, benzoic acid and phenylacetaldehyde. In both cases formation of benzaldehyde is relatively high. These catalysts are very active for the oxidation of methyl phenyl sulfide and diphenyl sulfide. The oxidation of diphenyl sulfide required at least H_2O_2 to diphenyl sulfide molar ratio of 3:1 to give 91.7% conversion in 7 h of reaction time. However, 94.3% conversion of methyl phenyl sulfide has been achieved within 3 h of contact time at a substrate to H_2O_2 ratio of 1:1. The catalytic activity of neat complexes using similar

molar concentration as that used for encapsulated complexes under above reaction conditions have also been tested for comparison. It has been observed that the corresponding neat complexes have shown equally good catalytic activities. However, higher turn over frequencies and recyclability make the zeolite-encapsulated complexes better than their neat analogues.

References

- [1] A. Butler, M.J. Clague, G.E. Meister, *Chem. Rev.* 94 (1994) 625–638.
- [2] V.M. Dembitsky, *Tetrahedron* 59 (2003) 4701–4720.
- [3] D. Rehder, G. Santoni, G.M. Licini, C. Schulzke, B. Meier, *Coord. Chem. Rev.* 237 (2003) 53–63.
- [4] C. Bolm, *Coord. Chem. Rev.* 237 (2003) 245–256.
- [5] G. Santoni, G. Licini, D. Rehder, *Chem. Eur. J.* 9 (2003) 4700–4708.
- [6] A. Butler, *Coord. Chem. Rev.* 187 (1999) 17–35.
- [7] A. Butler, in: J. Reedijk, E. Bouwman (Eds.), *Bioinorganic Catalysis*, 2nd ed., Marcel Dekker, New York, 1999 (Chapter 5).
- [8] V. Conte, F.D. Furiá, G. Licini, *Appl. Catal. A: Gen.* 157 (1997) 335–361.
- [9] A.G.J. Ligtenbarg, R. Hage, B.L. Feringa, *Coord. Chem. Rev.* 237 (2003) 89–101.
- [10] M.R. Maurya, M. Kumar, S.J.J. Titinchi, H.S. Abbo, S. Chand, *Catal. Lett.* 86 (2003) 97–105.
- [11] C.R. Jacob, S.P. Varkey, P. Ratnasamy, *Appl. Catal. A: Gen.* 168 (1998) 353–364.
- [12] C.R. Jacob, S.P. Varkey, P. Ratnasamy, *Micropor. Mesopor. Mater.* 22 (1998) 465–474.
- [13] Y.-F. Zhou, Z.-L. Bai, S.-Z. Chen, *Huadong Ligong Daxue Xuebao* 29 (2003) 138–143.
- [14] A. Kozlov, K. Asakura, Y. Iwasawa, *J. Chem. Soc., Faraday Trans.* 94 (1998) 809–816.
- [15] W.H. Quayle, G. Peeters, G.L. De Roy, E.F. Vansant, J.H. Lunsford, *Inorg. Chem.* 21 (1982) 2226–2231.
- [16] J. Poltowicz, K. Pamin, E. Tabor, J. Haber, A. Adamski, Z. Sojka, *Appl. Catal. A: Gen.* 299 (2006) 235–242.
- [17] P. Carr, B. Piggott, S.F. Wong, *Inorg. Chim. Acta* 123 (1986) 5–8.
- [18] M.R. Maurya, S. Sikarwar, *J. Mol. Catal. A: Chem.* 263 (2006) 175–185.
- [19] M.R. Maurya, S. Sikarwar, P. Manikandan, *Appl. Catal. A: Gen.* 315 (2006) 74–82.
- [20] A. Syamal, O.P. Singhal, *J. Inorg. Nucl. Chem.* 123 (1981) 2821–2825.
- [21] M.R. Maurya, A. Kumar, M. Ebel, D. Rehder, *Inorg. Chem.* 45 (2006) 5924–5937.
- [22] T. Joseph, D. Srinivas, C.S. Gopinath, S.B. Halligudi, *Catal. Lett.* 83 (2002) 209–214.
- [23] V. Hulea, E. Dumitriu, *Appl. Catal. A: Gen.* 277 (2004) 99–106.
- [24] C. Adhikary, D. Mal, K.-I. Okamoto, S. Chaudhury, S. Koner, *Polyhedron* 25 (2006) 2191–2197.
- [25] M.R. Maurya, A.K. Chandrakar, S. Chand, *J. Mol. Catal. A: Chem.* 263 (2007) 227–237.
- [26] C. Bowers, P.K. Dutta, *J. Catal.* 122 (1990) 271–279.
- [27] M. Salavati-Niasari, *Micropor. Mesopor. Mater.* 95 (2006) 248–256.
- [28] M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, *J. Mol. Catal. A: Chem.* 258 (2006) 327–333.