Zeolite-Y encapsulated metal complexes of oxovanadium(VI), copper(II) and nickel(II) as catalyst for the oxidation of styrene, cyclohexane and methyl phenyl sulfide

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Abstract

Oxovanadium(IV), copper(II) and nickel(II) complexes of Schiff base derived from salicylaldehyde and *o*-aminobenzyl alcohol (H$_2$sal-oaba) have been encapsulated in the nano-pores of zeolite-Y by flexible ligand method and characterised by metal analysis, spectroscopic (IR and electronic) studies, scanning electron micrographs, thermal analysis and X-ray diffraction patterns. The encapsulated complexes abbreviated here as [VO(sal-oaba)(H$_2$O)]-Y, [Cu(sal-oaba)(H$_2$O)]-Y and [Ni(sal-oaba)(H$_2$O)$_3$]-Y catalyse the oxidation of styrene, cyclohexane and methyl phenyl sulfide using H$_2$O$_2$ as oxidant in good yield. Styrene catalysed by [VO(sal-oaba)(H$_2$O)]-Y, [Cu(sal-oaba)(H$_2$O)]-Y under optimised reaction conditions gave five reaction products namely, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde, while [Ni(sal-oaba)(H$_2$O)$_3$]-Y gave benzaldehyde selectively. In the presence of *tert*-butylhydroperoxide all catalysts gave styrene oxide in major yield, though overall conversion has been found low (10–30%). The oxidation products of cyclohexane are cyclohexanone and cyclohexanol. A maximum of 93.2% conversion of methyl phenyl sulfide has been achieved with [VO(sal-oaba)(H$_2$O)]-Y using H$_2$O$_2$ as oxidant, where selectivity of sulfoxide was 96.9%. Other catalysts were inactive towards the oxidation of methyl phenyl sulfide while neat complex [VO(sal-oaba)] has been found to be equally active.
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1. Introduction

Transition metal complexes are well known for their catalytic activities in the oxidation as well as reduction of organic substrates and for the synthesis of fine chemicals. Their immobilisations on solid supports provide certain additional characteristic properties such as selectivity, thermal stability, and easy separation from the reaction mixture and recycle ability [1–4]. The immobilised materials are important to develop new environment friendly technologies. Immobilisation of metal complexes in the nano-cavity of zeolite is often termed as "zeolite encapsulated metal complexes" (ZEMC). Encapsulated molecules in zeolite are characterised by isolation from other molecules by zeolite lattice [5], low mobility [6] and steric restriction. These zeolite encapsulated metal complexes have been suggested as model compounds for enzyme mimicking and often referred to as "zeozymes" because zeolite replaces the protein mantle of the enzyme in the model compound [7]. The advantages of immobilised metal complexes promoted several research groups to investigate the catalytic properties of the complexes entrapped within the nano-cavities of zeolite-Y [8–13].

In this paper, we report the encapsulation of oxovanadium(IV), copper(II) and nickel(II) complexes of Schiff bases derived from salicylaldehyde and *o*-aminobenzyl alcohol (H$_2$sal-oaba, **I**; Scheme 1) in the nano-cavities of zeolite-Y by flexible ligand method. These zeolite encapsulated metal complexes have been screened for the oxidation of styrene, cyclohexane and thioanisol. Suitable reaction conditions have been optimised to obtain maximum oxidation of organic

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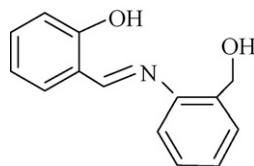
I: H$_2$sal-oaba

Scheme 1.

substrates. As neat copper(II) and oxovanadium(IV) complexes have tendency to stabilise as dimmer [14,15], encapsulation in the cavity of zeolite prevent their dimerisation and allow their stabilisation as monomeric active centre.

2. Experimental

2.1. Materials

Analytical reagents grade cyclohexane, 30% aqueous H$_2$O$_2$ (Ranbaxy, India), styrene (Acros Organics, New Jersey, USA), methyl phenyl sulfide (Alfa Aeaser, USA), o-aminobenzyl alcohol (Aldrich Chemical Company, USA), salicylaldehyde (sal), cupric nitrate, nickel nitrate, cupric acetate monohydrate, nickel acetate tetra hydrate (E. Merck, India) and vanadyl sulfate penta hydrate (Loba Chemie, India) were used as obtained. Na-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. H$_2$sal-oaba (**I**) [14], [Cu^{II}(sal-oaba)] (**2**) [15], [Ni^{II}(sal-oaba)(H$_2$O)$_3$] (**3**) [16] and M-Y (M = Cu(II), Ni(II) and OV(IV)) [17] were prepared as described in the literature.

2.2. Preparations

2.2.1. Preparation of [VO^{IV}(sal-oaba)])(**1**)

A stirred solution of H$_2$sal-oaba (1.355 g, 5 mmol) in dry methanol (50 ml) was treated with [VO(acac)$_2$] (1.33 g, 5 mmol) dissolved in dry methanol (25 ml) and the resulting reaction mixture was refluxed in an oil bath for 2 h. After cooling down to room temperature for over night, a greenish precipitate of **1** was filtered off, washed with methanol and dried in vacuum over silica gel. Yield: 80%.

2.2.2. Preparation of [VO^{IV}(sal-oaba)(H$_2$O)]-Y (**4**)

Ligand H$_2$sal-oaba (2.5 g) and OV(IV)-Y (1.0 g) were mixed in 50 ml of methanol and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was separated by filtration and then extracted with methanol using Soxhlet extractor to remove unreacted ligand from the cavities of the zeolite as well as located on the surface of the zeolite along with neat complexes, if any. The unreacted oxovanadium(IV) ions present in the zeolite was removed by stirring with aqueous 0.01 M NaCl solution (200 ml) for 8 h. The resulting solid was filtered and washed with distilled water until free from chloride ions. Finally, it was dried at 120 °C in an air oven for several hours.

2.2.3. Preparation of Cu^{II}(sal-oaba)(H$_2$O)]-Y (**5**) and [Ni^{II}(sal-oaba)(H$_2$O)$_3$]-Y (**6**)

Complexes [Cu^{II}(sal-oaba)(H$_2$O)]-Y (**5**) and [Ni^{II}(sal-oaba)(H$_2$O)$_3$]-Y (**6**) were prepared following essentially the same procedure out lined for [VO(sal-oaba)(H$_2$O)]-Y by replacing OV(IV)-Y with Cu(II)-Y or Ni(II)-Y.

2.3. Physical methods and analysis

IR spectra were recorded as KBr pellet on a Nicolet NEXUS Aligent 1100 series FT-IR spectrophotometer after grinding the sample with KBr. Electronic spectra of zeolite encapsulated metal complexes were recorded in Nujol using a Shimadzu 1601 UV–vis spectrophotometer by layering a mull sample to inside of one of the cuvettes while keeping another one layered with Nujol as reference. Electronic spectra of neat complexes were recorded in methanol. Thermogravimetric analyses of pure as well as encapsulated complexes were carried out using TG Stanton Redcroft STA 780. The metal contents were measured using inductively coupled plasma (ICP; Labtam 8440 Plasmalab) after leaching the metal ions with conc. nitric acid and diluting with distilled water (for copper and nickel) or very dilute aqueous KOH solution (for vanadium) to specific volumes. X-ray powder diffractograms of solid catalysts were recorded using a Bruker AXS D8 Advance X-ray powder diffractometer with a Cu Kα target. All catalysed reaction products were analysed using Thermoelectron Gas Chromatograph fitted with HP-1 capillary column (30 m × 0.25 mm × 0.25 μm) and FID detector.

2.4. Catalytic activity

2.4.1. Oxidation of styrene

The catalytic oxidation of styrene was carried out in a 50 ml two necked flask fitted with septum and water circulated condenser using a general procedure for all catalysts. In a typical reaction, an aqueous 30% H$_2$O$_2$ or 70% *tert*-butylhydroperoxide (TBHP) (20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH$_3$CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The encapsulated 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. The identities of the products were confirmed by GC–MS.

2.4.2. Oxidation of cyclohexane

Aqueous 30% H$_2$O$_2$ (2.28 g, 20 mmol), cyclohexane (0.84 g, 10 mmol) and catalyst (0.040 g) were mixed in 5 ml of CH$_3$CN and the reaction mixture was heated at 70 °C with continuous stirring in an oil bath for 2 h. The formed reaction products were analysed using gas chromatograph as mentioned above.

2.4.3. Oxidation of methyl phenyl sulfide (thioanisol)

Aqueous 30% H$_2$O$_2$ (0.57 g, 5 mmol), thioanisol (0.62 g, 5 mmol) and catalyst (0.015 g) were mixed in 20 ml of CH$_3$CN and the reaction mixture was stirred at room temperature. The

progress of the reaction was monitored as mentioned above and the identities of various products were confirmed by GC–MS.

3. Results and discussion

3.1. Characterisation of catalysts

Encapsulation of complexes, [VO^{IV}(sal-oaba)(H$_2$O)], [Cu^{II}(sal-oaba)(H$_2$O)] and [Ni^{II}(sal-oaba)(H$_2$O)$_3$] in the nano-cavities of zeolite-Y was carried out by flexible ligand method where ligand enters slowly into the cavity through the zeolite pores due to its flexible nature and reacts with previously exchanged metal ions. The resulting complexes are big enough in size and do not escape from the nano-cavity of zeolite. The purification of crude mass by Soxhlet extraction using excess of methanol removed excess free ligand that remained uncomplexed in the cavities of the zeolite along with the neat complex formed on the surface of the zeolite, if any. The uncomplexed metal ions remained, if any, in the cavity of zeolite were removed by exchanging back with aqueous 0.01 M NaCl solutions. The percentages of metal contents determined before and after encapsulation by inductively coupled plasma along with their expected formula and colour are presented in Table 1. As crude mass was Soxhlet 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.

Neat complexes [VO(sal-oaba)], [Cu(sal-oaba)] and [Ni(sal-oaba)(H$_2$O)$_3$] have also been prepared by reacting H$_2$sal-oaba with suitable metal precursors. These complexes have previously been prepared and well characterised [14–16]. The dimeric square pyramidal structure for [VO(sal-oaba)], dimeric square planar structure for [Cu(sal-oaba)] and monomeric octahedral structure for [Ni(sal-oaba)(H$_2$O)$_3$] have been reported. A detailed spectroscopic study (IR and electronic) for these complexes has, therefore, been only considered to compare their properties with the corresponding encapsulated complexes. The encapsulated complexes are expected to have monomeric structure. This is based on the fact that the diagonal distance of the known crystal structure [MoO$_2$(sal-ohyba)·CH$_3$OH] (H$_2$sal-ohyba = Schiff base derived from salicylaldehyde and *o*-hydroxybenzylamine) with isomeric ligand system is ca. 10 Å [18] and thus dimerisation of copper(II) and oxovanadium(IV) complexes will be prevented due to size constraints. The coordination of water molecule(s) to complete the coordination geometry of these monomeric species is expected as excess
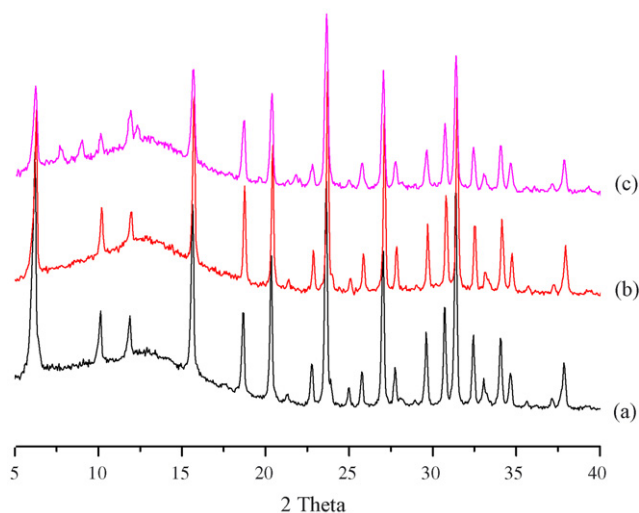

Fig. 1. XRD pattern of (a) Na-Y, (b) Cu-Y and (c) [Cu(sal-oaba)(H$_2$O)]-Y.

intra-zeolite water is always present in zeolite-encapsulated complexes. Alternatively, oxygen present in the super cages of the zeolite framework may also coordinate to complete the coordination geometry.

3.2. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na-Y, M-Y (M = OV(IV), Cu(II) and Ni(II)) and encapsulated metal complexes were recorded at 2θ values between 5° and 70°. The XRD patterns of representative metal exchanged zeolite and zeolite encapsulated metal complexes along with Na-Y are presented in Fig. 1. The diffraction patterns of encapsulated metal complexes, M-Y and Na-Y are essentially similar except a slight change in the intensity of the bands in encapsulated complexes. These observations indicate that the framework of the zeolite has not undergone any significant structural change during encapsulation. This is expected as ligand being flexible in nature enters slowly through pores of the zeolite and fits nicely in the cavity upon coordination with the metal ions. Two new but week peaks due to neat complexes were detected in the encapsulated zeolite at 2θ values of 7.7 and 9.05 due to 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. A representative TGA profile of [Cu(sal-oaba)(H$_2$O)]-Y is presented in Fig. 2. The thermograms of catalysts, [VO(sal-oaba)(H$_2$O)]-Y (**4**), [Cu(sal-oaba)(H$_2$O)]-Y (**5**) and [Ni(sal-oaba)(H$_2$O)$_3$]-Y (**6**) indicate their decomposition in three steps, though these steps are overlapping. The exothermic removal of just trapped water of ca. 4.2% (in **4**), ca. 4.7% (in **5**) or ca. 3.3% (in **6**) occurs up to 150 °C, while an exothermic weight loss of ca. 6.3% (in **4**), ca. 8.0% (in **5**) or ca. 6.1% (in **6**) associated with removal of intra-zeolite water occurs in the temperature range 150–350 °C. As all encapsulated complexes have one or more water molecules coordinated, their removal in

Table 1
Chemical composition, physical and analytical data

No.	Catalyst	Colour	Metal content (wt.%)
1	OV(IV)-Y	Light green	4.6
2	Cu(II)-Y	Pale blue-green	7.6
3	Ni(II)-Y	Pale-green	6.8
4	[VO(sal-oaba)(H$_2$O)]-Y	Light green	2.6
5	[Cu(sal-oaba)(H$_2$O)]-Y	Light green	3.3
6	[Ni(sal-oaba)(H$_2$O)$_3$]-Y	Yellow	1.5

Table 2
Thermogravimetric analysis data of catalysts

Catalyst	Temperature range (°C)	Weight loss (%)	Group lost
[VO(sal-oaba)(H$_2$O)]-Y	70–150	4.2	H$_2$O
	150–350	6.3	nH$_2$O
	350–800	13.1	L
[Cu(sal-oaba)(H$_2$O)]-Y	70–150	4.7	H$_2$O
	150–350	8.0	nH$_2$O
	350–800	15.6	L
Ni(sal-oaba)(H$_2$O)$_3$]-Y	70–150	3.3	H$_2$O
	150–350	6.1	nH$_2$O
	350–800	9.1	L
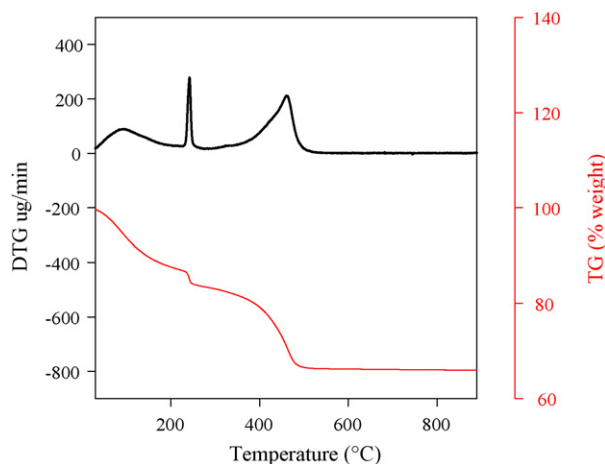
Fig. 2. TG (red line) and DTG (black line) profiles of [Cu(sal-oaba)(H$_2$O)]-Y.

this step is also expected. The third step involves the slow but exothermic weight loss of ca. 13.1% (in **4**), ca. 15.6% (in **5**) or ca. 9.1% (in **6**) in a wider temperature range due to decomposition of the metal complexes. A low weight loss percentage in higher temperature range is in agreement with the low percentage of metal content obtained for encapsulated complexes.

3.4. Spectral studies

Table 3 lists IR and electronic spectral data of ligand and complexes. 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 their neat complexes showed essentially similar bands. Comparison of the spectra of these

catalysts with the ligand provides evidence for the coordinating mode of ligand in catalysts.

The IR spectrum of ligand H$_2$sal-oaba exhibits a medium intensity band around 2700 cm^{-1} due to intra-molecular hydrogen bonding. Absence of this band in the spectra of encapsulated complexes indicates the destruction of the hydrogen bond followed by the coordination of phenolic and alcoholic oxygen after deprotonation. The sharp band appearing at 1617 cm^{-1} due to the ν(C=N) (azomethine), shifts to lower wave number and appears at 1610–1615 cm^{-1}. This indicates the coordination of azomethine nitrogen to the metal ions. Neat complex [VO(sal-oaba)] exhibits a sharp band at 985 cm^{-1} due to the ν(V=O) stretch [14], while in zeolite encapsulated vanadium complex location of band due to V=O structure has not been possible due to the appearance of a strong and broad band at ca. 1000 cm^{-1} due to zeolite frame work.

Electronic spectral studies of H$_2$sal-oaba and its complexes, [VO(sal-oaba)], [Cu(sal-oaba)] and [Ni(sal-oaba)(H$_2$O)$_3$] have been studied in detail by Syamal et al. [14–16]. Their spectral data also presented in Table 3 are similar to those reported. As they have recorded diffused reflectance spectra of complexes, a partial difference in their positions has been noted in ligand bands. Similarly, we have observed only one d–d band for complexes [VO(sal-oaba)] and [Cu(sal-oaba)] at 525 and 600 nm, respectively. No such d–d band(s) could be observed for [Ni(sal-oaba)(H$_2$O)$_3$]. Electronic spectra of encapsulated complexes recorded in nujol exhibit essentially similar spectral features but their intensities are relatively poor. The expected d–d bands in these complexes could not be located possibly due to their poor loading. Fig. 3 reproduces the electronic spectra of these encapsulated complexes.

3.5. Catalytic activity studies

3.5.1. Oxidation of styrene

Oxidation of styrene, catalysed by [VO(sal-oaba)(H$_2$O)]-Y, [Cu(sal-oaba)(H$_2$O)]-Y and [Ni(sal-oaba)(H$_2$O)$_3$]-Y, using H$_2$O$_2$ as an oxidant gave styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde (Scheme 2). Some of these products have also been identified by others [8,19,20]. Recently, the formation of all these products have been observed when polymer-supported catalyst, PS-[VO(sal-ohyba)(DMF)] was applied [21].

Reaction conditions have been optimised considering [VO(sal-oaba)(H$_2$O)]-Y as a representative catalyst and varying different reaction parameters viz. amount of catalyst and

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

| Compound	IR (cm^{-1})	λ_{max} (nm)
H$_2$sal-oaba	1617, 1565, 1482, 1455, 1179, 1032	212, 228, 269, 338
[VO(sal-oaba)(H$_2$O)]-Y	1637, 1612, 1584, 1450	221, 263, 404
[Cu(sal-oaba)(H$_2$O)]-Y	1645, 1615, 1585, 1437, 787	222, 240, 291, 402
[Ni(sal-oaba)(H$_2$O)$_3$]-Y	1646, 1612, 1441, 784	217, 264, 401
[VO(sal-oaba)]	1610, 1580, 1464, 1441, 1152, 985	272, 307, 398, 525
[Cu(sal-oaba)]	1612, 1579, 1441, 1027, 752, 642	208, 262, 295, 405, 600
[Ni(sal-oaba)(H$_2$O)$_3$]	1612, 1580, 1112, 759, 652	209, 233, 296, 404
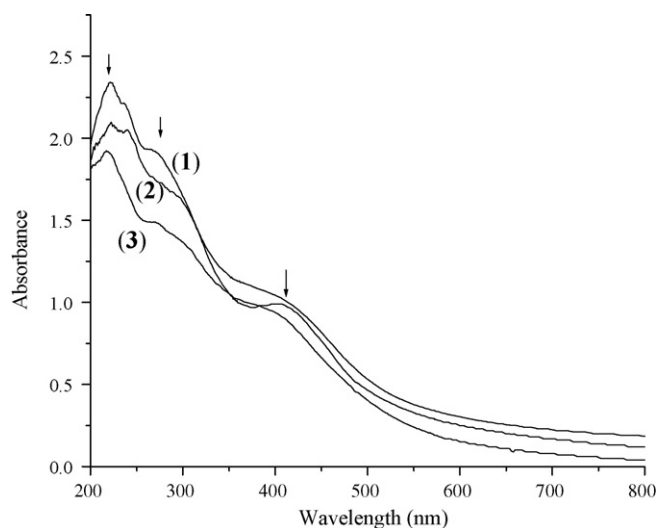
Fig. 3. Electronic spectra of [VO(sal-oaba)(H$_2$O)]-Y (**1**), [Cu(sal-oaba)(H$_2$O)]-Y (**2**) and [Ni(sal-oaba)(H$_2$O)$_3$]-Y (**3**).

Fig. 4. Effect of amount of oxidant on the oxidation of styrene.

oxidant, and temperature of the reaction mixture to achieve maximum oxidation of styrene. Amount of H$_2$O$_2$ has considerable effect on the oxidation of styrene as has been demonstrated considering four different styrene to H$_2$O$_2$ molar ratios at the fixed amount of styrene (1.04 g, 10 mmol), catalyst (0.025 g), CH$_3$CN (20 ml) and temperature (80 °C). As shown in Fig. 4, the conversion of styrene improved from 44.2% to 56.1% on increasing the styrene to H$_2$O$_2$ molar ratio from 1:1 to 1:1.5. This conversion further improved to 88.7% at 1:2 (styrene to H$_2$O$_2$) molar ratio and finally a decreasing trend was observed at 1:2.5 ratio. The reason for the decreasing trend may be due to dilution of the reaction mixture by the presence of larger amount of water molecules in H$_2$O$_2$ solution. Thus, it is clear that the 1:2 molar ratio is the best one to obtain the optimum styrene conversion of 88.7% in 6 h reaction time.

Similarly, four different amounts of catalyst viz. 0.015, 0.025, 0.035 and 0.050 g were considered while keeping a fixed amount of styrene (1.04 g, 10 mmol), aqueous H$_2$O$_2$ (2.28 g, 20 mmol)
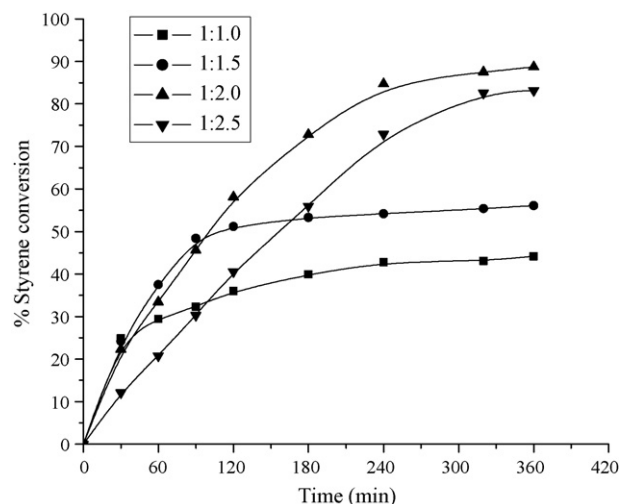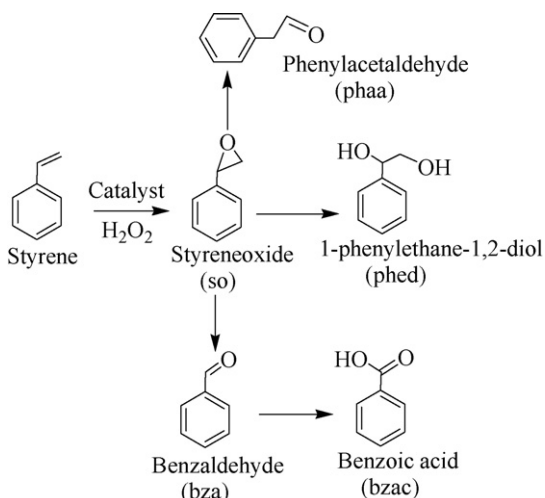
and CH$_3$CN (20 ml), and reaction was carried out at 80 °C. Fig. 5 presents the results of percent styrene conversion as a function of time. It is seen from the figure that 0.015 g catalyst gave only 51.2% conversion, while 0.025 g catalyst has shown a maximum conversion of 88.7%. Further increment of catalyst amount to 0.035 g marginally improved this conversion while a decreasing trend has been observed with 0.050 g catalyst. Thus, at the expense of H$_2$O$_2$, 0.025 g catalyst may be considered sufficient enough to carry out the reaction with good conversion. The reason for reduced activity at higher catalyst dose may possibly be attributed to adsorption/chemisorption of two reactants on separate catalyst particles, thereby reducing the chance to interact.

Fig. 6 illustrates the effect of temperature on the oxidation of styrene at the above optimised conditions. Amongst three different temperatures (50, 65 and 80 °C) studied, catalytic reaction at 80 °C had the maximum oxidation of styrene. Also, the reaction reaches to its equilibrium in less time at this temperature.
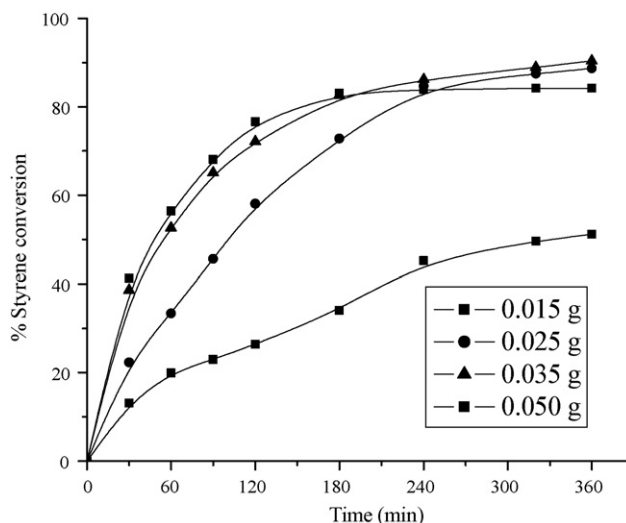

Scheme 2.
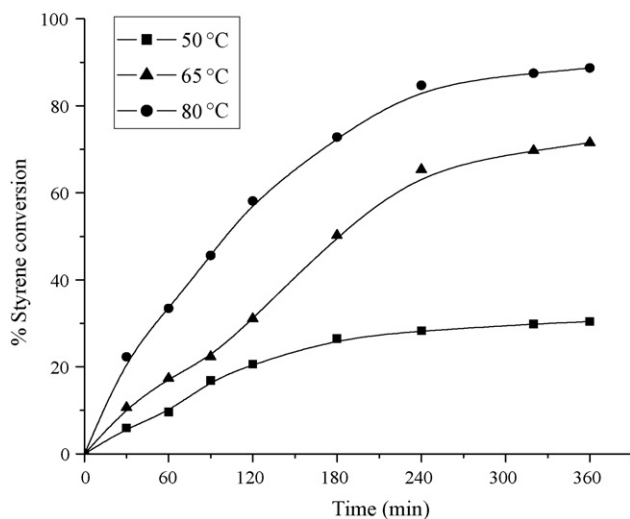

Fig. 5. Effect of amount of catalyst on the oxidation of styrene.

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

Fig. 8. Effect of catalysts [VO(sal-oaba)(H₂O)]-Y (a), [Cu(sal-oaba)(H₂O)]-Y (b), [Ni(sal-oaba)(H₂O)₃]-Y (c), [VO(sal-oaba)] (d), [Cu(sal-oaba)] (e) and [Ni(sal-oaba)(H₂O)₃]-Y (f) on the oxidation of styrene using TBHP as oxidant.

Thus, for the maximum oxidation of 10 mmol of styrene other required parameters as concluded were: [VO(sal-oaba)(H₂O)]-Y (0.025 g), H_2O_2 (2.28 g, 20 mmol), CH_3CN (20 ml) and temperature (80 °C).

After acquiring the optimised reaction conditions for [VO(sal-oaba)(H₂O)]-Y with H_2O_2 as oxidant, other catalysts, e.g. [Cu(sal-oaba)(H₂O)]-Y and [Ni(sal-oaba)(H₂O)₃]-Y were also tested under the same conditions, i.e. 10 mmol styrene, 20 mmol 30% H_2O_2, 0.025 g catalyst and 20 ml CH_3CN at 80 °C for the oxidation of styrene. The results presented in Fig. 7 show that the percentage conversion follow the order: [VO(sal-oaba)(H₂O)]-Y (88.7%) > [Cu(sal-oaba)]-Y (23.4%) > [Ni(sal-oaba)(H₂O)₃]-Y (6.6%). Catalytic activites of neat complexes have also been tested using same mole concentration of complex as taken in case of encapsulated complexes and the reaction performed under similar conditions as mentioned above. As shown in Fig. 7, these complexes have shown

very poor catalytic activity. However, they also maintain the same order of efficiency. Thus, the catalytic activity of the encapsulated complexes is better than their respective neat analogues.

tert-Butylhydroperoxide was also used as oxidant for the oxidation of styrene. The oxidation of styrene at the styrene/TBHP molar ratio of 1:2 at the fixed amount of styrene (1.04 g, 10 mmol), CH_3CN (20 ml) and reaction temperature (80 °C) gave a maximum of 19.7% conversion while higher as well as lower molar ratios always gave lower conversions. The catalytic activities of other catalysts using TBHP as oxidant under the above conditions have been carried out and results are presented in Fig. 8. It is clear from the figure that [Cu(sal-oaba)(H₂O)]-Y has a maximum of 30.2% conversion which is followed by [VO(sal-oaba)(H₂O)]-Y with 19.7% and [Ni(sal-oaba)(H₂O)₃]-Y showing only 10.3% conversion. Under similar conditions, neat complexes were also tested and as shown in Fig. 8, they have shown even poorer performance.

Table 4 analyses the selectivity of various products using H_2O_2 as oxidant, while Table 5 gives details using TBHP as oxidant. In case of [VO(sal-oaba)(H₂O)]-Y, the selectivity of various reaction products follow the order: benzaldehyde > 1-phenylethane-1,2-diol > benzoic acid > styreneoxide > phenylacetaldehyde, while for [Cu(sal-oaba)(H₂O)]-Y catalyst, the order is: benzaldehyde > styreneoxide > phenyl acetaldehyde > benzoic acid. As high as 15.8% selectivity of an important reaction product styreneoxide has only been obtained with [Cu(sal-oaba)(H₂O)]-Y while other catalysts have shown very poor selectivity towards styreneoxide. Catalyst, [Ni(sal-oaba)(H₂O)₃]-Y was highly selective towards the formation of benzaldehyde and gave only small amount of other products. A highest yield of benzaldehyde is possibly due to further oxidation of styreneoxide formed in the first step by a nucleophilic attack of H_2O_2 on styreneoxide followed by cleavage of the intermediate hydroperoxistyrene (Scheme 3). Oxidative cleavage of the styrene side chain double bond via a radical mechanism may also produce benzaldehyde. High amount of water present in H_2O_2
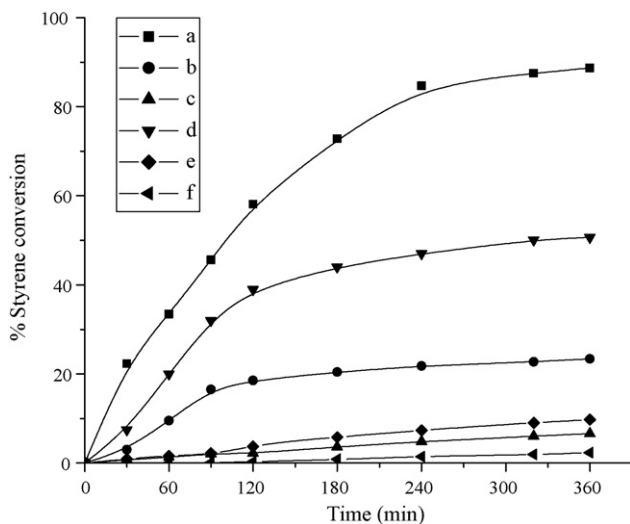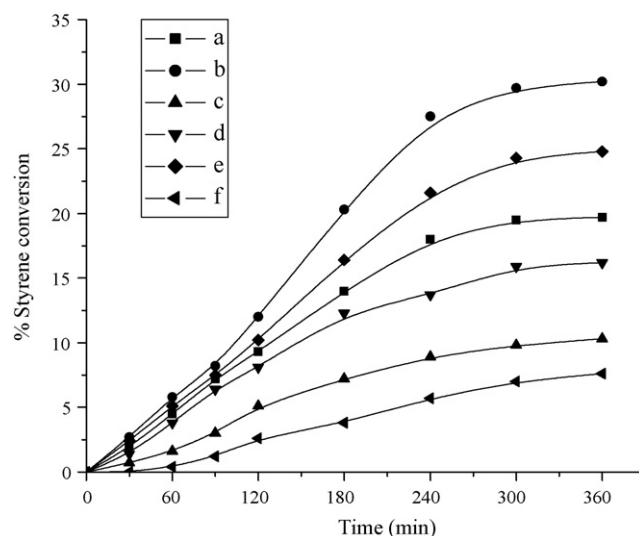

Fig. 7. Catalytic activity of [VO(sal-oaba)(H₂O)]-Y (a), [Cu(sal-oaba)(H₂O)]-Y (b), [Ni(sal-oaba)(H₂O)₃]-Y (c), [VO(sal-oaba)] (d), [Cu(sal-oaba)] (e) and [Ni(sal-oaba)(H₂O)₃]-Y (f) for the oxidation of styrene using H_2O_2 as oxidant.

Table 4
Products selectivity and percent conversion of styrene after 6 h of reaction time using H_2O_2 as oxidant

Catalyst	%Conversion	TOF[a] (h^{-1})	%Product selectivity[b]					
			so	bza	phed	bzac	phaa	Other
[VO(sal-oaba)(H2O)]-Y	88.7	696.0	6.8	58.8	24.1	6.7	2.1	1.5
[Cu(sal-oaba) (H2O)]-Y	23.4	180.1	15.8	68.2	0	9.1	5.7	1.2
[Ni(sal-oaba)(H2O)3]-Y	6.6	103.3	0	98.4	0	0	0	1.6
[VO(sal-oaba)]	50.7	397.8	6.9	74.2	8.9	4.1	4.9	1.0
[Cu(sal-oaba)]	9.5	73.1	9.7	77.4	0	9.6	2.2	1.1
[Ni(sal-oaba)(H2O)3]-Y	2.3	36.0	0	98.8	0	0	0	1.2

[a] TOF h^{-1} (turnover frequency): moles of substrate converted per mole of metal (in the solid state catalyst) per hour.
[b] For abbreviations see Scheme 2.

Table 5
Products selectivity and percent conversion of styrene with TBHP after 6 h of reaction time

Catalyst	%Conversion	TOF (h^{-1})	%Product selectivity					
			so	bza	phed	bzac	phaa	Other
[VO(sal-oaba)(H2O)]-Y	19.7	154.6	60.4	31.3	3.9	1.5	0	2.9
[Cu(sal-oaba) (H2O)]-Y	30.2	232.4	71.0	21.3	2.0	0	1.4	4.3
[Ni(sal-oaba)(H2O)3]-Y	10.3	161.2	43.4	49.2	0	0	0	7.4
[VO(sal-oaba)]	16.2	127.1	57.4	31.7	4.3	0	0.8	0.9
[Cu(sal-oaba)]	24.8	190.9	60.9	20.5	8.5	0	2.6	7.5
[Ni(sal-oaba)(H2O)3]	7.6	118.9	39.6	52.5	0	0	0	7.9

is partly responsible for the possible hydrolysis of styreneoxide to 1-phenylethane-1,2-diol. Other products in limited percentage, e.g. benzoic acid may form through further oxidation of benzaldehyde. Similarly, the formation of phenylacetaldehyde may occur through isomerisation of styreneoxide.

Using TBHP, a milder oxidant, the reaction is highly selective towards the formation of styreneoxide with all neat as well as encapsulated complexes. Its selectivity order for encapsulated complex is: [Cu(sal-oaba)(H2O)]-Y (71.0%) > [VO(sal-oaba)(H2O)]-Y (60.4%) > [Ni(sal-oaba)(H2O)3]-Y (43.4%). This is followed by the formation of benzaldehyde. The selectivity of other two or three reaction products has no definite trend. Table 5 summarises the results along with the turn over frequency for conversion of styrene after 6 h of reaction time using TBHP as oxidant.

Catalytic potentials of these complexes compare well with similar encapsulated complexes. About 34.8% conversion of styrene was noted with zeolite-Y encapsulated [VO(salphen)] (H2salphen = Schiff base derived from salicylaldehyde and *o*-phenylenediamine) using 70% *tert*-butylhydroperoxide as an oxidant [8]. Zeolite-Y encapsulated

catalyst [VO2(sal-ambmz)]-Y and [Cu(sal-ambmz)Cl]-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 oxidant [17]. Catalyst [Mn(salen)]-Y (H2salen = Schiff base derived from salicylaldehyde and ethane-1,2-diaminoethene) exhibits ca. 30% conversion of styrene using molecular oxygen as an oxidant in excess of *tert*-butylhydroperoxide as initiator [19]. The observed conversions for zeolite-Y encapsulated complexes [Mn(Cl2-haacac)Cl]-NaY (89.7%) [9], [Mn((NO2)2-haacac)Cl]-NaY (96.9%) (H2haacac = bis(2-hydroxyanil)acetylacetone) [22] with *tert*-butylhydroperoxide as initiator and air as oxidant are close to the one reported in Table 5. Zeolite encapsulated catalyst [Mn(3-MeOsalen)]-Y, [Mn(3-MeOsalpn)]-Y and [Mn(salpn)]-Y (H2salpn = bis(salicylaldehyde)-1,3-diaminopropane) exhibits 17%, 8.7% and 7.4% conversions, respectively, using *tert*-butylhydroperoxide as oxidant [23]. About 80% conversion of styrene was observed with polymer-supported catalyst PS-K[VO2(sal-ohyba)]. The selectivity of styreneoxide with all these catalysts is always low [21].

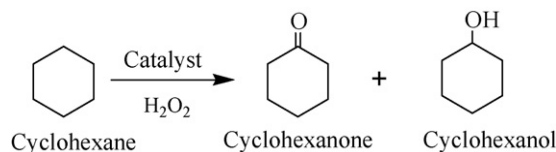### 3.5.2. Oxidation of cyclohexane

The activity tests of the prepared catalysts were also carried out for the oxidation of cyclohexane. After several trials, the best-suited reaction conditions for the oxidation of 10 mmol of cyclohexane were concluded as follows: catalyst (0.040 g), CH3CN (20 ml) and reaction temperature (70 °C). Under the optimised reaction conditions, the encapsulated complexes, [VO(sal-oaba)(H2O)]-Y and [Cu(sal-oaba)(H2O)]-Y have been tested for the oxidation of cyclohexane and the results obtained after 2 h of reaction time are summarised in Table 6. A maximum of 45.8% conversion has been achieved with [Cu(sal-
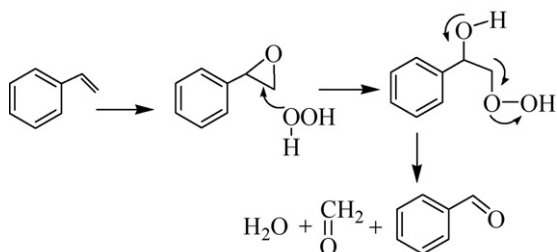
Scheme 3.

Table 6
Effect of different catalysts on the oxidation of cyclohexane and product selectivity

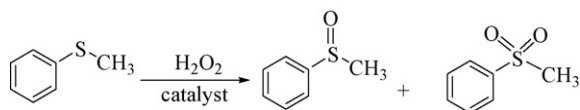| Catalyst	%Conversion	TOF (h^{-1})	Product selectivity (%)		
			O (cyclohexanone)	OH (cyclohexanol)	Other
[Cu(sal-oaba)(H$_2$O)]-Y	45.8	220.3	50.7	44.8	4.5
[VO(sal-oaba)(H$_2$O)]-Y	14.8	72.6	56.7	38.5	4.8
[Cu(sal-oaba)]	11.4	54.8	42.2	51.3	6.5
[VO(sal-oaba)]	4.7	23.1	40.4	57.4	2.2

Scheme 4.

oaba)(H$_2$O)]-Y, while [VO(sal-oaba)(H$_2$O)]-Y gave only 21.0% conversion with major products of cyclohexenol and cyclohexanone as shown in Scheme 4. The selectivity of these products varies in the order: cyclohexanone > cyclohexanol. A small amount (ca. 5%) of an unidentified product has also been observed and is possibly cyclohexane-1,2-diol. The formation of cyclohexane-1,2-diol in better yield along with other products has recently been identified when [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y were used as catalyst [17].

Same mole concentrations of neat complexes, as used for encapsulated ones, have shown very poor result under above reaction conditions (see Table 6). However, the selectivity of cyclohexenol is better than cyclohexanone. The turns over frequencies for these complexes are also relatively less than that of the encapsulated ones.

3.5.3. 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 by aqueous 30% H$_2$O$_2$ has been carried out using [VO(sal-oaba)(H$_2$O)]-Y, [Cu(sal-oaba)(H$_2$O)]-Y and [Ni(sal-oaba)(H$_2$O)$_3$]-Y as catalyst. Two oxidation products as shown by Scheme 5 have been obtained.

In order to get optimum reaction conditions, amount of oxidant and catalyst were varied while carrying the reaction at room temperature. The effect of H$_2$O$_2$ concentration on the oxidation of methyl phenyl sulfide is illustrated in Fig. 9. Three different methyl phenyl sulfide/aqueous 30% H$_2$O$_2$ molar ratios viz. 1:0.5, 1:1 and 1:2 were considered at the fixed amounts of methyl phenyl sulfide (0.62 g, 5 mmol) and catalyst [VO(sal-

oaba)(H$_2$O)]-Y (0.015 g) in 20 ml of CH$_3$CN. Increasing the ratio from 1:0.5 to 1:1 increased the conversion from 42.5% to 93.2% in 3 h of reaction time. Further increasing the ratio to 1:2, though marginally improved the conversion, this molar ratio influenced to reduce the completion of the reaction time considerably. However, at the expense of H$_2$O$_2$, methyl phenyl sulfide/aqueous 30% H$_2$O$_2$ molar ratio of 1:1 has been considered the most appropriate to proceed.

Similarly, four different amount of catalyst (viz. 0.005, 0.015, 0.025 and 0.035 g) were considered for 5 mmol of methyl phenyl sulfide under above mentioned reaction conditions and the results obtained are presented in Fig. 10 as function of reaction time. It is clear from the figure that 0.015 g catalyst is sufficient enough to give 93.2% conversion in 3 h of reaction time. Higher amounts of catalyst influence only to reduce the equilibrium time of the reaction. The selectivity percentages of methyl phenyl sulfoxide and methyl phenyl sulfone at the methyl phenyl sulfide:aqueous 30% H$_2$O$_2$ molar ratio of 1:1 are 96.9% and 3.1%, respectively.

A blank reaction under similar conditions, i.e. methyl phenyl sulfide (5 mmol), aqueous 30% H$_2$O$_2$ (5 mmol) and CH$_3$CN (20 ml), resulted in 37.5% conversion where 69.3% selectivity was registered for sulfoxide and 30.7% for sulfone. Thus, the complex [VO(sal-oaba)(H$_2$O)]-Y not only enhanced the percent conversion of methyl phenyl sulfide, it also improved the selectivity for sulfoxide. The catalytic performances of these encapsulated complexes compare well with the data recently
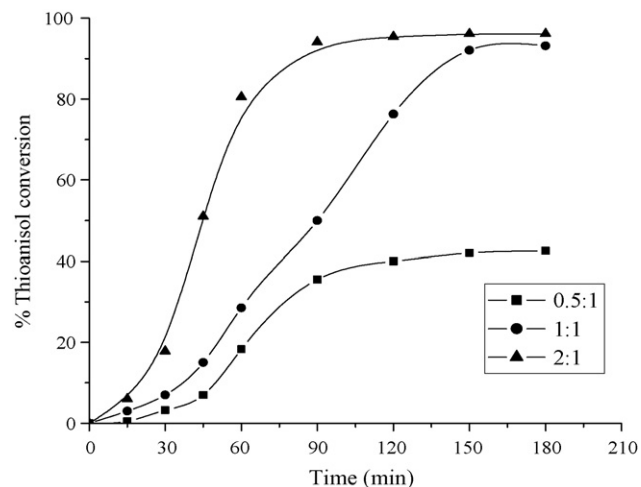

Scheme 5.

Fig. 9. Effect of H$_2$O$_2$:thioanisol molar ratio on the oxidation of thioanisol.
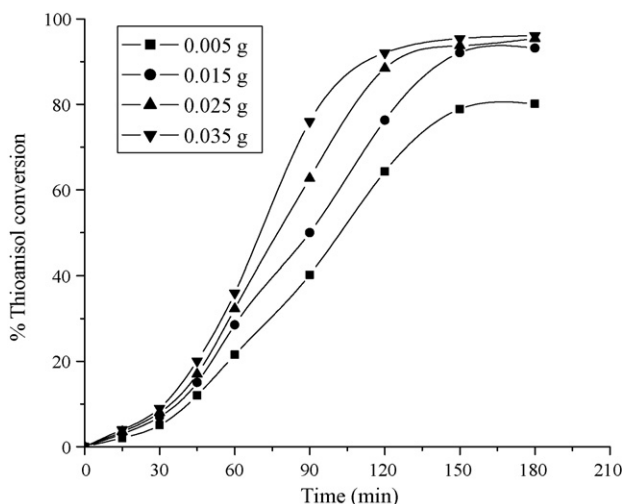
Fig. 10. Effect of amount of catalyst on the oxidation of thioanisol.

reported for zeolite-Y encapsulated [VO$_2$(sal-ambmz)]-Y which exhibits 97% conversion [24].

After acquiring the optimised reaction conditions for [VO(sal-oaba)(H$_2$O)]-Y, other catalyst, e.g. [Cu(sal-oaba)(H$_2$O)]-Y and [Ni(sal-oaba)(H$_2$O)$_3$]-Y were also tested. Unfortunately these catalysts did not show appreciable effect on the conversion of methyl phenyl sulfide and thus, they seem to be catalytically inactive for sulfide oxidation.

Neat complexes, [VO(sal-oaba)], [Cu(sal-oaba)] and [Ni(sal-oaba)(H$_2$O)$_3$] were also tested for catalytic activity using same mole concentration as zeolite encapsulated one under above mentioned optimised conditions. Again, [Cu(sal-oaba)] and [Ni(sal-oaba)(H$_2$O)$_3$] did not show any catalytic activity, while [VO(sal-oaba)] has shown a maximum of 91.4% conversion. This catalytic activity is comparable to that of encapsulated vanadium complex. The selectivity of the products is also comparable. Table 7 summarises products selectivity and conversion details for vanadium complexes.

3.6. Possible reaction pathway of the catalysts

We have tried to establish the possible reaction pathway of the catalysts during catalytic action by reacting methanolic solution of neat complexes [VO(sal-oaba)] and [Cu(sal-oaba)] with H$_2$O$_2$ dissolved in methanol and monitoring the changes by electronic absorption spectroscopy. Thus, the treatment of ca. 10^{-4} M solution of [VO(sal-oaba)] in methanol with one drop portions of 30% H$_2$O$_2$ dissolved in minimum amount of methanol caused the slow disappearance of 307 and 398 nm bands while the inten-
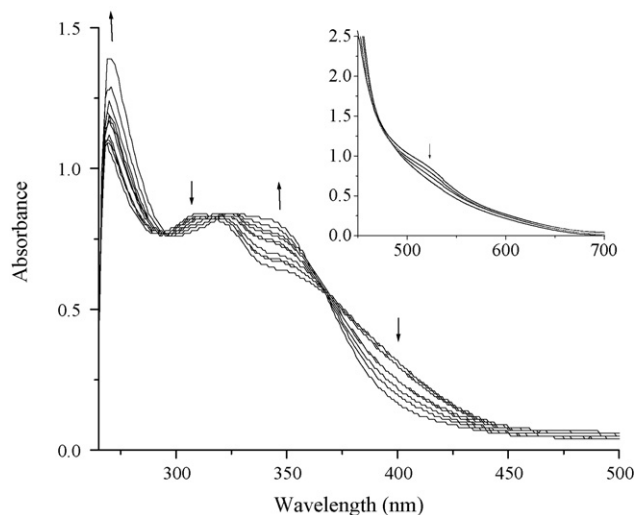

Fig. 11. Titration of [VO(sal-oaba)] with H$_2$O$_2$. The spectra were recorded after successive addition of one drop portions of H$_2$O$_2$ in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of [VO(sal-oaba)] in methanol. The plots presented in inset were recorded in DMSO.

Fig. 12. Titration of [Cu(sal-oaba)] with H$_2$O$_2$. The spectra were recorded after successive addition of one drop portions of H$_2$O$_2$ in minimum amount of methanol to 10 ml of ca. 10^{-4} M solution of [Cu(sal-oaba)] in methanol. The plots presented in inset were recorded in DMSO.
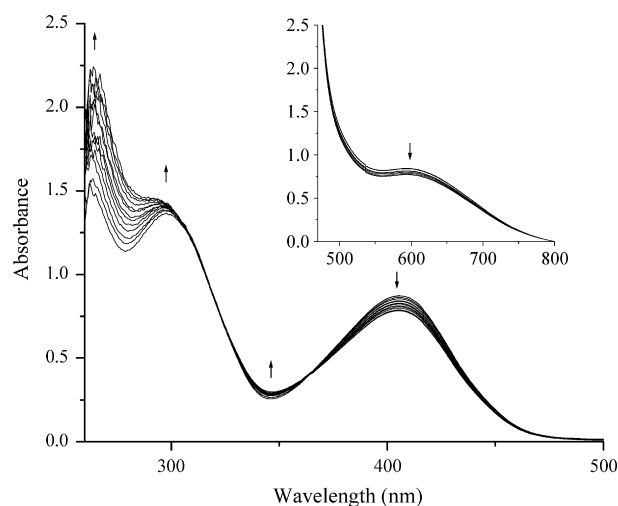
sity of 350 nm bands slowly increased with slight shift at 330 nm. The band appearing at 272 nm mainly gained intensity (Fig. 11). The weak broad d–d band at 525 nm slowly disappeared (see inset of Fig. 11). Similarly, titration of [Cu(sal-oaba)] with H$_2$O$_2$ resulted in the partial decrease in the intensities of 405 (see

Table 7
Percent conversion of thioanisol and selectivity of sulfoxide and sulfone formation at room temperature after 3 h of contact time

Catalyst	%Conversion	TOF (h^{-1})	%Selectivity	
			Methyl phenyl sulfoxide	Methyl phenyl sulfone
[VO(sal-oaba)(H$_2$O)]-Y	93.2	597.8	96.9	3.1
[VO(sal-oaba)]	91.4	586.2	98.4	1.6
Without catalyst	37.5	–	69.3	30.7

inset of Fig. 12) and 600 nm bands while partial increase in the intensity of 296 nm band with broadening (Fig. 12). The band appearing at 262 nm gained intensity. All these suggest the formation of peroxo species on the interaction of [VO(sal-oaba)] and [Cu(sal-oaba)] with H_2O_2. The in situ generation of peroxo species has been observed previously by oxovanadium(IV) and copper(II) complexes on interaction with oxidants like H_2O_2 and *tert*-butylhydroperoxide [24]. This in situ generated peroxo species finally transfer oxygen to the substrates to give oxidized products. Thus, the reversible intermediate formation of facile peroxo species may be responsible for the catalytic performance of the encapsulated species. This is further supported by the fact that isolation of peroxovanadium(V) complex of H_2sal-oaba by reacting [VO(sal-oaba)] with H_2O_2 always failed and ended up with the starting complex [VO(sal-oaba)].

4. Conclusions

The zeolite encapsulated metal complexes, [VO(sal-oaba)(H$_2$O)]-Y, [Cu(sal-oaba)(H$_2$O)]-Y and [Ni(sal-oaba)(H$_2$O)$_3$]-Y have been prepared and characterised. Catalytic activities of these complexes have been tested for the oxidation of styrene, cyclohaxene and methyl phenyl sulfide using H_2O_2 as oxidant. Styrene catalysed by [VO(sal-oaba)(H$_2$O)]-Y gives five reaction products, styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde. Except, 1-phenylethane-1,2-diol, all four products have also been obtained with [Cu(sal-oaba)(H$_2$O)]-Y. Styreneoxide, an important product has been obtained only in poor yield, while the yield of benzaldehyde is highest. Complex, [Ni(sal-oaba)(H$_2$O)$_3$]-Y gave benzaldehyde selectively, though conversion is only 6.6%. With 45.8% conversion of cyclohexane by [Cu(sal-oaba)(H$_2$O)]-Y, the selectivity of two products follow the order: cyclohexanone (50. 7%) > cyclohexanol (44.8%). [VO(sal-oaba)(H$_2$O)]-Y has shown only 14.8% conversion. A maximum of 93.2% conversion of methyl phenyl sulfide has been achieved with [VO(sal-oaba)(H$_2$O)]-Y using H_2O_2 as oxidant, where selectivity of sulfoxide and sulfone are 96.9% and 3.1%, respectively. Other catalysts have been found inactive towards the oxidation of methyl phenyl sulfide. Neat complex, [VO(sal-oaba)] has shown equally good catalytic activity. All heterogeneous catalysts are stable and free from leaching as has been confirmed by testing the filtrate for the corresponding metal ion. They are recyclable at least up to two cycles.

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