

Oxovanadium(IV) and copper(II) complexes of 1,2-diaminocyclohexane based ligand encapsulated in zeolite-Y for the catalytic oxidation of styrene, cyclohexene and cyclohexane

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Abstract

N,N'-Bis(salicylidene)cyclohexane-1,2-diamine (H₂sal-dach) reacts with oxovanadium(IV) and copper(II) exchanged zeolite-Y in refluxing methanol to yield the corresponding zeolite-Y encapsulated metal complexes, abbreviated herein as [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y. Spectroscopic studies (IR, electronic and ¹H NMR), thermal analysis, scanning electron micrographs (SEM) and X-ray diffraction patterns have been used to characterise these complexes. These encapsulated complexes catalyse the oxidation, by H₂O₂, of styrene, cyclohexene and cyclohexane efficiently in good yield. Under the optimized conditions, the oxidation of styrene catalysed by [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y gave 94.6 and 21.7% conversion, respectively, where styreneoxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde being the major products. Oxidation of cyclohexene catalysed by these complexes gave cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as major products. Conversion of cyclohexene achieved was 86.6% with [VO(sal-dach)]-Y and 18.1% with [Cu(sal-dach)]-Y. A maximum of 78.1% conversion of cyclohexane catalysed by [Cu(sal-dach)]-Y and only 21.0% conversion by [VO(sal-dach)]-Y with major reaction products of cyclohexanone, cyclohexanol and cyclohexane-1,2-diol have been obtained.

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Keywords: Catalysts; Zeolite-Y encapsulated complexes; Oxidation reaction; Oxidation of styrene; Oxidation of cyclohexene; Oxidation of cyclohexane

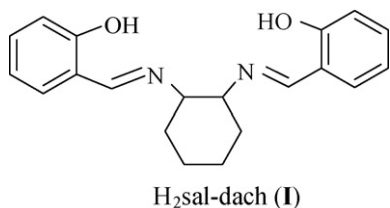
1. Introduction

Modern catalytic sciences have played an important role in the development of heterogeneous catalysts for new chemical technologies. Amongst heterogeneous catalysts, zeolite encapsulated metal complexes (ZEMC) hold a key place as they have also been suggested as model compounds for enzyme mimicking [1]. This is because zeolites may replace the protein mantle of the enzyme in the model compound. A molecule encapsulated in the zeolite cages is characterised by steric restriction and if the size of the molecule is comparable to the zeolite cage, the molecule in the cage may show interesting properties, which are not encountered under ordinary conditions. All these advantages prompted

several research groups to investigate the catalytic properties of the complexes entrapped within the super cages of zeolite-Y [2–14].

The oxyfunctionalization of inexpensive hydrocarbons to produce more valuable organic compounds such as alcohols, aldehydes, and ketones, requires the selective oxidation of strong C–H bonds. Alcohols and ketones are important intermediate materials for the manufacture of many important products, such as, fiber, drugs and fragrance. Chun Jin et al. have encapsulated transition metal tetrahydro-Schiff base complexes in the zeolite-Y and studied their catalytic potentialities for the oxidation of cycloalkanes [15]. Complex [Cu(salen)] catalyses, by peroxide, the oxidation of cyclohexane in moderate yield [16]. Zeolite-Y encapsulated manganese(II) complexes have been used for the oxidation of cyclohexene by *tert*-butylhydroperoxide [17]. Transition metal complexes catalysed oxidation of styrene into a variety of products such as epoxides, carbonyl compounds, diols and oxidative cleavage

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Scheme 1.

products of C–C has received much attention primarily due to interest in selective and partial oxidations [18–22].

In this paper, we report herein the encapsulation of oxovanadium(IV) and copper(II) complexes of 1,2-diaminocyclohexane based ligand H₂sal-dach (I, Scheme 1) in the cavity of zeolite-Y by the flexible ligand method. These zeolite encapsulated complexes have, therefore, been screened as catalysts for the oxidation of styrene, cyclohexene and cyclohexane.

2. Experimental

2.1. Materials

Analytical reagents grade cyclohexane and 30% aqueous H₂O₂ were obtained from Ranbaxy, India. Cupric nitrate, cupric chloride, salicylaldehyde, 1,2-diaminocyclohexane were obtained from E. Merck, India. Vanadyl sulfate penta hydrate from Loba Chemie, India and styrene from Acros Organics, New Jersey, USA were used as such. 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. [VO(acac)₂] was prepared following literature procedure [23].

2.2. Preparations

2.2.1. Preparation of H₂sal-dach

A solution of 1,2-diaminocyclohexane (1.44 g, 10 mmol) in 10 ml methanol was added drop wise to a methanolic solution of salicylaldehyde (2.56 g, 10 mmol in 20 ml) and the reaction mixture was heated under reflux on a water bath for 2 h. After cooling to room temperature, the yellow precipitate of H₂sal-dach was filtered off, washed with hot methanol and dried in vacuo over silica gel. Yield: 80%. Anal. found C, 74.04%; H, 6.97%; N, 8.51%. Calcd. for C₂₀H₂₂N₂O₂ (322): C, 74.53%; H, 6.83%; N, 8.70%. ¹H NMR (δ in ppm): 13.68, 13.34 (2:1, s, 2H, OH), 8.58, 8.49 (2:1, s, 2H, –CH=N–), 7.44(d), 7.31–7.32(m), and 6.81–6.90(m) (8H, aromatic), 3.68 (d, 2H, –CH– of cyclohexyl), 1.76–1.87 and 1.56–1.57 (complex m, 8H, –CH₂– of cyclohexyl).

2.2.2. Preparation of M-Y

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

2.2.3. Preparation of [Cu^{II}(sal-dach)]-Y (1) and [VO^{IV}(sal-dach)]-Y (2): a general method

Both encapsulated complexes were prepared using a flexible ligand method, therefore, a general method is outlined here. An amount of 1.0 g of Cu-Y or OV-Y and 2.5 g ligand were mixed in 60 ml of methanol in a round bottom flask and the reaction mixture was refluxed for 15 h in an oil bath with stirring. The resulting material was filtered and extracted with methanol using Soxhlet extractor to remove excess ligand that remained uncomplexed in the cavities of the zeolite as well as located on the surface of the zeolite along with neat complexes, if any. The remaining uncomplexed metal ions in zeolite were removed by stirring with aqueous 0.01 M NaCl solution (200 ml) 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.

2.2.4. Preparation of [VO^{IV}(sal-dach)]

The ligand H₂sal-dach (1.61 g, 5 mmol) dissolved in 20 ml of methanol was added to a solution of [VO(acac)₂] (1.33 g, 5 mmol) dissolved in 10 ml of methanol and the reaction mixture was refluxed for 2 h. During this period green solid of [VO(sal-dach)] slowly separated out. After cooling the mixture, it was filtered off, washed with methanol and dried in vacuo over silica gel. Yield 65%. Anal. found C, 62.23%; H, 5.42%; N, 7.18%. Calcd. for C₂₀H₂₀N₂O₃V (381): C, 62.99%; H, 5.25%; N, 7.35%.

2.2.5. Preparation of [Cu^{II}(sal-dach)]

A solution of Cu(CH₃COO)₂·H₂O (1.0 g, 5 mmol) dissolved in 20 ml of methanol was added to a hot solution of H₂sal-dach (1.61 g, 5 mmol) in 20 ml of methanol, and the reaction mixture was refluxed on a water bath for 2 h. Violet solid of [Cu(sal-dach)] slowly separated out within a few hours period on cooling the solution at ambient temperature. This was filtered off, washed with methanol and dried in vacuo over silica gel. Yield 68%. Anal. found C, 62.28%; H, 5.13%; N, 7.41%. Calcd. for C₂₀H₂₀N₂O₂Cu (383.54): C, 62.57%; H, 5.21%; N, 7.30%.

2.3. Physical methods and analysis

Electronic spectra of zeolite encapsulated metal complexes were recorded in Nujol using Shimadzu 1601 UV–vis spectrophotometer by layering a small 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. IR spectra were recorded as KBr pellet on a Nicolet NEXUS Aligent 1100 series FT-IR spectrophotometer after grinding the sample with KBr. ¹H NMR spectrum of H₂sal-dach was recorded on Bruker 500 MHz machine in DMSO-*d*₆. Thermogravimetric analyses of pure as well as encapsulated complexes were carried out using TG Stanton Redcroft STA 780. The metal content were measured using inductively coupled plasma (ICP; Labtam 8440 plasmalab) after leaching the metal ions with concentrated nitric acid and diluting with distilled water (for copper) or very dilute aque-

Table 1
Chemical composition, physical and analytical data

S. no.	Catalyst	Colour	Metal content (wt.%)	Langmuir surface area (m ² /g)
1	OV(IV)-Y	Light green	4.58	439
2	Cu(II)-Y	Yellow	7.60	752
3	[VO(sal-dach)]-Y	Light green	0.84	241
4	[Cu(sal-dach)]-Y	Pale blue-green	2.61	489

ous KOH solution (for vanadium) to specific volumes. X-ray powder diffractograms of solid catalyst were recorded using a Bruker AXS D8 Advance X-ray Powder Diffractometer with a Cu K α target. All catalyzed reaction products were analysed using Thermoelectron Gas Chromatograph fitted with 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 (Perkin-Elmer, Clarus 500). Scanning electron micrographs (SEM) of catalyst were recorded on a Leo Instrument Model 435VP. The sample 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.

2.4. Catalytic activity

2.4.1. Oxidation of styrene

The catalytic oxidation of styrene was carried out using complexes, [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y in a 50 ml flask fitted with a water circulated condenser. In a typical reaction, an aqueous solution of 30% H₂O₂ (2.28 g, 20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH₃CN 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 identity by GC–MS.

2.4.2. Oxidation of cyclohexene

The catalytic oxidation of cyclohexene was also carried out using both the catalysts. In a typical reaction, an aqueous solution of 30% H₂O₂ (2.28 g, 20 mmol), cyclohexene (0.82 g, 10 mmol) and catalyst (0.035 g) were mixed in 20 ml of CH₃CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. The progress of the reaction was monitored as mentioned above and identity of the various products confirmed by GC–MS.

2.4.3. Oxidation of cyclohexane

Aqueous solution of 30% H₂O₂ (2.28 g, 20 mmol), cyclohexane (0.84 g, 10 mmol) and catalyst (0.035 g) were mixed in 5 ml of CH₃CN and the reaction mixture was heated at 70 °C with continuous stirring in an oil bath for 2 h. The formation of the reaction products and their identity were confirmed as mentioned above.

3. Results and discussion

3.1. Characterisation of catalysts

Synthesis of complexes [VO(sal-dach)] and [Cu(sal-dach)] encapsulated in the nano-cavity of zeolite-Y involved the exchange of oxovanadium(IV) and copper(II) ions with Na(I) of Na-Y followed by reaction of metal exchanged zeolite-Y with H₂sal-dach in solution. Here, ligand entered into the cavity of zeolite-Y due to its flexible nature and interacted with metal ions. The formation of ligand was confirmed by elemental analysis and ¹H NMR spectroscopy (cf. experimental section). 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, the metal ion content found after encapsulation is only due to the presence of metal complexes in the nano-cavity of the zeolite-Y. The molecular formula of the complexes are based on the neat complexes [VO(sal-dach)] and [Cu(sal-dach)] that have also been prepared by reacting the corresponding suitable metal precursor with the ligand and characterised.

Table 1 lists the surface area of VO(IV)-Y, Cu(II)-Y and their encapsulated complexes. As expected, encapsulation of transition metal complexes in zeolite-Y led to an apparent reduction in the surface area and pore volume. Thus, a reduction by about 45 and 35% in surface area was observed upon inclusion of [VO(sal-dach)]-Y and [Cu(H₂sal-dach)]-Y, respectively. Nevertheless, the decreasing degree depends on the amount of incorporated complexes as well as their molecular size and geometrical conformation inside the zeolitic host.

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 (a) Cu(II)-Y and (b) [Cu(sal-dach)]-Y are presented in Fig. 1.

3.1.1. 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 2 θ values between 5° and 70°. The XRD patterns of Na-Y, Cu(II)-Y and zeolite encapsulated complex [Cu(sal-dach)]-Y are presented in Fig. 2. An essentially similar pattern in Na-Y, metal ions exchanged zeolite and encapsulated metal complexes was 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 signifi-

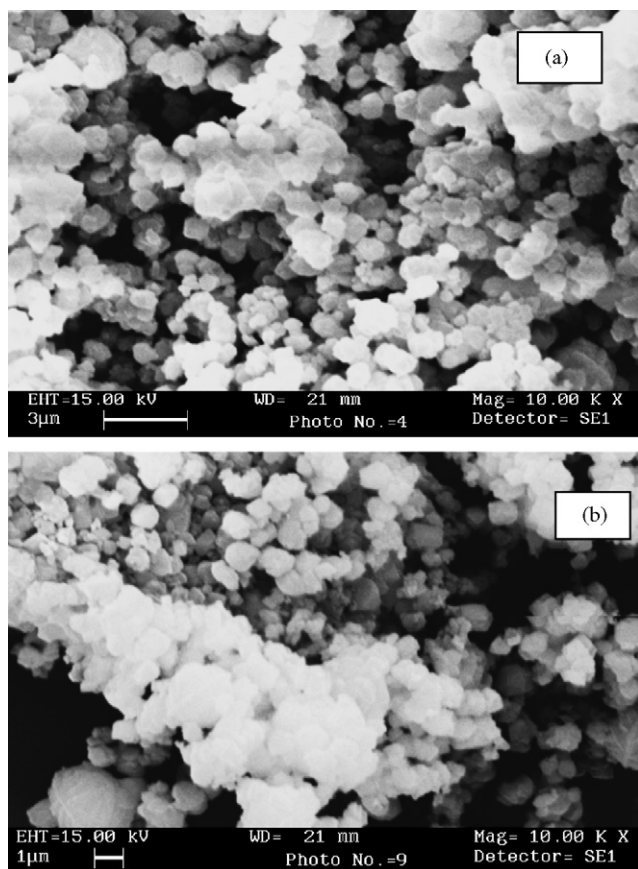


Fig. 1. Scanning electron micrograph of (a) Cu-Y and (b) [Cu(sal-dach)]-Y.

cant 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.

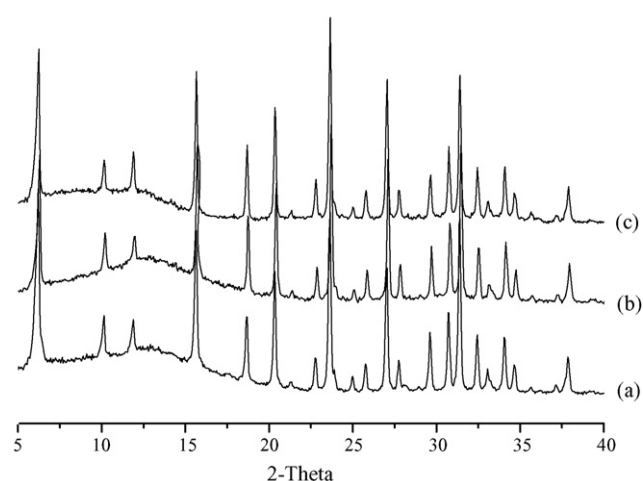


Fig. 2. XRD pattern of (a) Na-Y, (b) Cu-Y and (c) [Cu(sal-dach)]-Y.

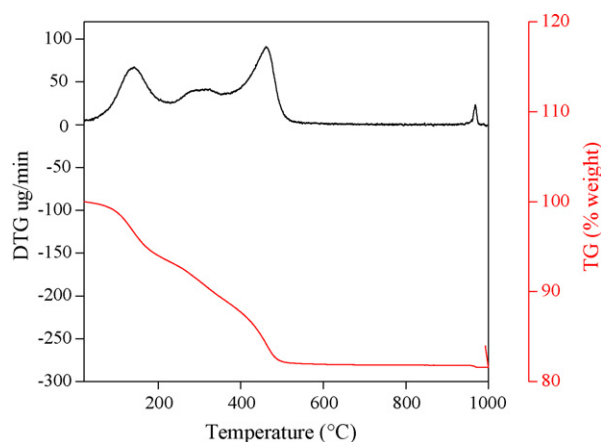


Fig. 3. TG (red line) and DTG (black line) profile of [Cu(sal-dach)]-Y.

3.1.2. Thermogravimetric analysis

The TG and DTG profile of one representative complex [Cu(sal-dach)]-Y is reproduced in Fig. 3. Thermograms of catalysts, [VO(sal-dach)]-Y (**1**) and [Cu(sal-dach)]-Y (**2**) indicate that their decomposition occurs in three steps, though these steps are overlapping. The removal of just trapped water of ca. 6.2% (in **1**) or ca. 5% (in **2**) occurs up to ca. 170 °C, while an exothermic weight loss of ca. 7.3% (in **1**) or ca. 6.6% (in **2**) associated with removal of intrazeolite water occurs in the temperature range 170–350 °C. The third step involves the slow but exothermic weight loss of ca. 7.5% (in **1**) or ca. 7.3% (in **2**) in a wider temperature range (350–800 °C) due to decomposition of the chelating ligand. The loss in small percentage indicates the insertion of only small amount of metal complexes in the cavity of the zeolite-Y. This is in agreement with the low percentage of metal content obtained for encapsulated complexes.

3.1.3. IR spectral studies

A partial list of IR spectral data is presented in Table 2. 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 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 H₂sal-dach exhibits a broad band in the 2450–2750 cm⁻¹ due to extensive hydrogen bonding between phenolic hydrogen and nitrogen of azomethine group. Absence of this band in the spectra of encapsulated complexes indicates the destruction of the hydrogen bond followed by the coordination of phenolic oxygen after deprotonation. The sharp band appearing at 1629 cm⁻¹ due to $\nu(\text{C}=\text{N})$ (azomethine), shifts to

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

Compound	IR (cm ⁻¹) $\nu(\text{C}=\text{N})$	λ_{max} (nm)
H ₂ sal-dach	1629	207, 226, 268, 337
[VO(sal-dach)]-Y	1621	222, 281, 357
[Cu(sal-dach)]-Y	1624	217, 261, 346
[VO(sal-dach)]	1618	236, 278, 360, 568
[Cu(sal-dach)]	1622	228, 273, 354, 560

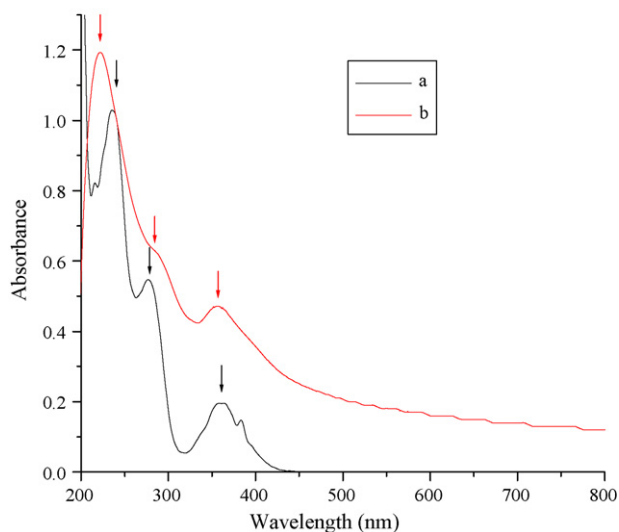


Fig. 4. Electronic spectra of [VO(sal-dach)] (a) and [VO(sal-dach)]-Y (b).

lower wave number and appears at 1618–1624 cm^{-1} . This indicates the involvement of azomethine nitrogen in coordination. The presence of multiple bands at 2840–2935 cm^{-1} in ligand and its complexes with slight shift suggests the presence of CH_2 group of cyclohexane in ligand as well as its complexes. Neat complex [VO(sal-dach)] exhibit a sharp band at 990 cm^{-1} due to $\nu(\text{V}=\text{O})$ stretch, while in zeolite encapsulated vanadium complex location of bands due to $\nu(\text{V}=\text{O})$ structure has not been possible due to appearance of a strong and broad band at ca. 1000 cm^{-1} due to zeolite frame work.

3.1.4. Electronic spectral studies

The electronic spectral data of ligand and complexes are also presented in Table 2. The electronic spectral profiles of [VO(sal-dach)] and [VO(sal-dach)]-Y are reproduced in Fig. 4 while that of [Cu(sal-dach)] and [Cu(sal-dach)]-Y are in Fig. 5. The electronic spectrum of ligand $\text{H}_2\text{sal-dach}$ exhibits three bands at 337, 268 and 207 nm and these are assigned due to $n \rightarrow \pi^*$,

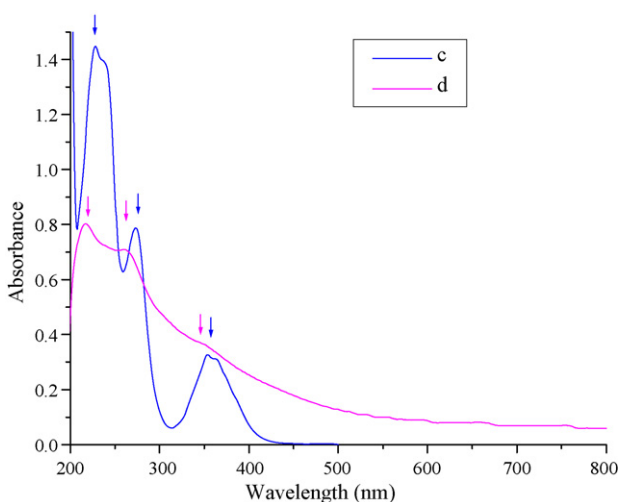
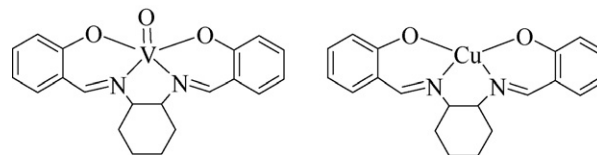


Fig. 5. Electronic spectra of [Cu(sal-dach)] (c) and [Cu(sal-dach)]-Y (d).



Scheme 2. Proposed structures for complexes.

$\pi \rightarrow \pi^*$ and $\phi \rightarrow \phi^*$ transitions, respectively. All these bands shift to higher wave length side indicating the restructuring of the ligand after coordination to the metal ion. Appearance of a weak band due to ligand to metal transition underneath of $n \rightarrow \pi^*$ transition make this band broad. While no band could be located in further higher wave length region due to expected d–d transition in the encapsulated complexes; neat complexes exhibit at least one broad band at 568 nm (in [VO(sal-dach)]) or at 560 nm (in [Cu(sal-dach)]).

On the basis of all these studies, the structures as shown in Scheme 2 have been proposed for these complexes.

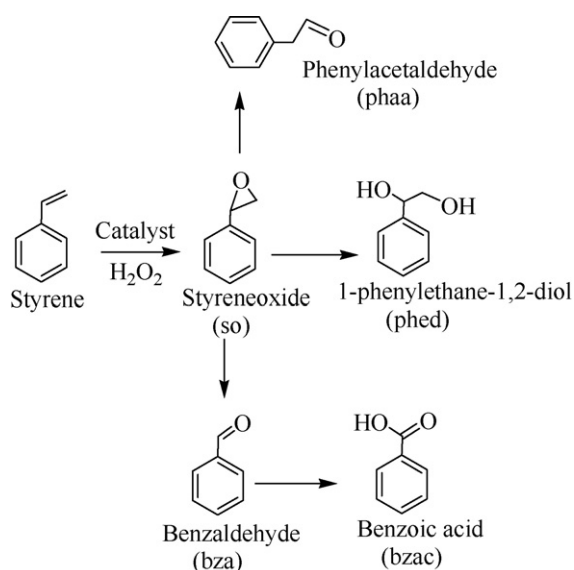
3.2. Catalytic activity studies

3.2.1. Oxidation of styrene

The oxidation of styrene, catalysed by [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y, was carried out using H_2O_2 as an oxidant to give styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenyl acetaldehyde along with only minor amounts of unidentified products. The formation of all these products is represented by Scheme 3. These are common products and have been identified by others as well [18–20].

In search of suitable reaction conditions to achieve the maximum oxidation of styrene, the effect of three different reaction parameters viz. oxidant concentration, catalyst concentration and temperature of the reaction were studied.

The effect of H_2O_2 concentration on the oxidation of styrene is illustrated in Fig. 6. Three different $\text{H}_2\text{O}_2/\text{styrene}$ molar ratios 1:1, 2:1 and 3:1 were considered while keeping the fixed amount



Scheme 3.

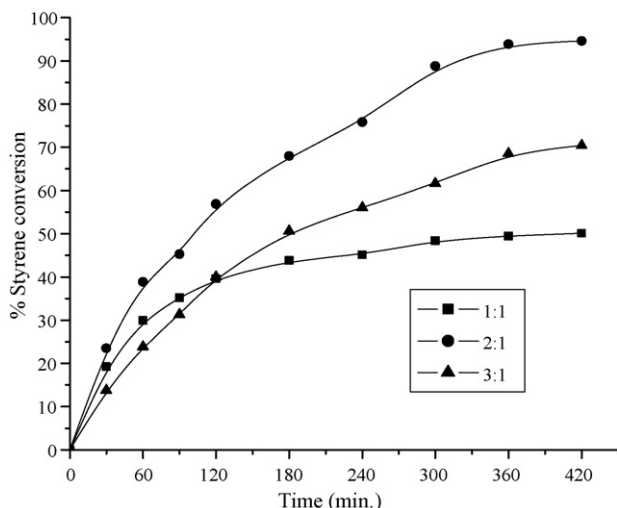


Fig. 6. Effect of H_2O_2 concentration (H_2O_2 : styrene) on oxidation of styrene.

of styrene (1.04 g, 10 mmol) and catalyst (0.025 g) in 20 ml of CH_3CN at 80°C . Increasing the H_2O_2 /styrene ratio from 1:1 to 2:1 increases the conversion from 65.6 to 94.6%. Further increasing the ratio to 3:1, speeds up the initial conversion but over all conversion rolls back to 70.4%. The reason for this may be due to the dilution of the reaction mixture by the presence of larger amount of water molecules in H_2O_2 solution. It is, therefore, clear that the 2:1 molar ratio is best one to obtain the maximum styrene conversion of 94.6% in 7 h reaction time. The effect of amount of catalyst on the oxidation of styrene was also studied. Five different amounts of [VO(sal-dach)]-Y viz. 0.015, 0.020, 0.025, 0.035 and 0.050 g were considered while keeping a fixed amount of styrene (1.04 g, 10 mmol) and H_2O_2 (2.28 g, 20 mmol) in 20 ml of CH_3CN and the reaction was carried out at 80°C . As illustrated in Fig. 7, the conversion increases on increasing the amount of catalyst and a maximum of 94.6% conversion has been achieved with 0.025 g of catalyst. Further increment of catalyst amount results in lower conversion.

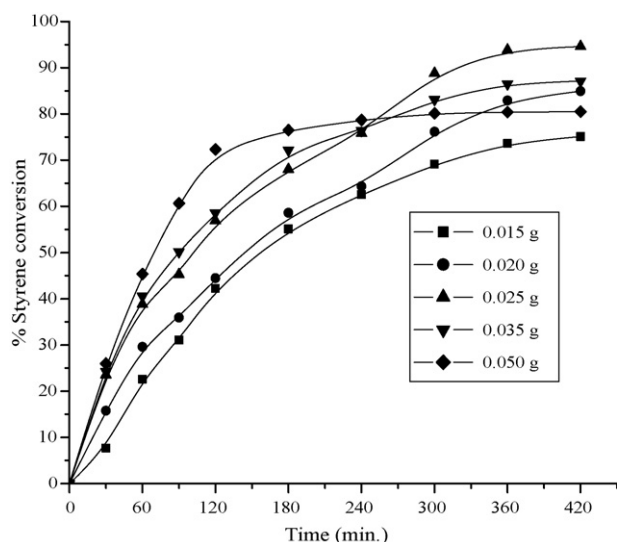


Fig. 7. Effect of amount of catalyst on the oxidation of styrene.

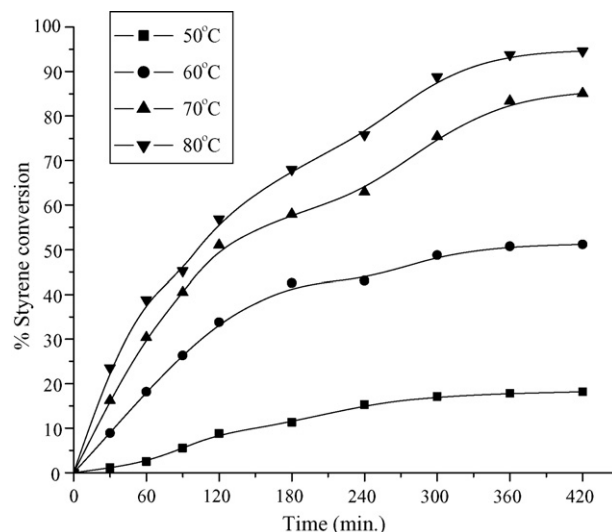


Fig. 8. Effect of temperature on the oxidation of styrene.

Therefore, an amount of 0.025 g catalyst may be considered as optimum to obtain the maximum conversion of styrene. Fig. 8 illustrates the effect of temperature on the oxidation of styrene. Amongst the four different temperatures of 50, 60, 70 and 80°C , running the reaction at 80°C while keeping the other conditions optimised as above gave a highest conversion of 94.6%. A total of 7 h was required to obtain equilibrium. Thus, for the maximum oxidation of 10 mmol of styrene other required reagents as concluded were: [VO(sal-dach)]-Y (0.025 g), H_2O_2 (2.28 g, 20 mmol) in CH_3CN (20 ml) and temperature (80°C).

Under these optimized reaction conditions, catalyst [Cu(sal-dach)]-Y has shown a maximum of only 21.7% conversion after 7 h of reaction time with four reaction products: styreneoxide, benzoic acid, benzaldehyde and phenyl acetaldehyde while, as mentioned earlier, [VO(sal-dach)]-Y has given one additional product, 1-phenylethane-1,2-diol. Table 3 compares their selectivity data along with the conversion percentage and turn over frequency (TOF) after 7 h of reaction time. It is clear from the data that the selectivity of the various products obtained from catalyst [VO(sal-dach)]-Y follow the order: benzaldehyde (54.5%) > 1-phenylethane-1,2-diol (22.5%) > benzoic acid (8.9%) > styrene oxide (7.6%) > phenyl acetaldehyde (4.9%). Catalyst [Cu(sal-dach)]-Y gave slightly different selectivity order. Here, the selectivity of styrene oxide is better (12.9%) while the highest selectivity of benaldehyde (67.3%) is maintained. Catalytic activity of neat complexes [VO(sal-dach)] and [Cu(sal-dach)] have also been tested. Fig. 9 presents the profiles of conversion percentage of styrene as a function of time for these catalysts including their encapsulated analogues. Neat complexes also exhibit good catalytic activity. This is due to the presence of more number of metal centres in homogeneous catalyst than heterogeneous one within the same weight of catalyst. The yields of various reaction products are also very much similar to their encapsulated analogues. However, their turns over frequencies are extremely low as compared to their encapsulated analogues.

Table 3
Products selectivity and percent conversion of styrene after 7 h of reaction time

Catalyst (25 mg)	Conversion (%)	TOF (h ⁻¹) ^a	Product selectivity (%) ^b					
			so	bza	phed	bzac	phaa	Others
[VO(sal-dach)]-Y	94.6	327.5	7.6	54.2	22.5	8.9	4.9	1.9
[Cu(sal-dach)]-Y	21.7	30.1	12.9	67.3	–	7.1	12.0	0.8
[VO(sal-dach)]	39.4	8.7	3.9	69.0	16.2	5.2	0.6	0.9
[Cu(sal-dach)]	31.8	6.9	13.8	58.4	–	12.9	13.1	0.8

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

^b For abbreviations see Scheme 3.

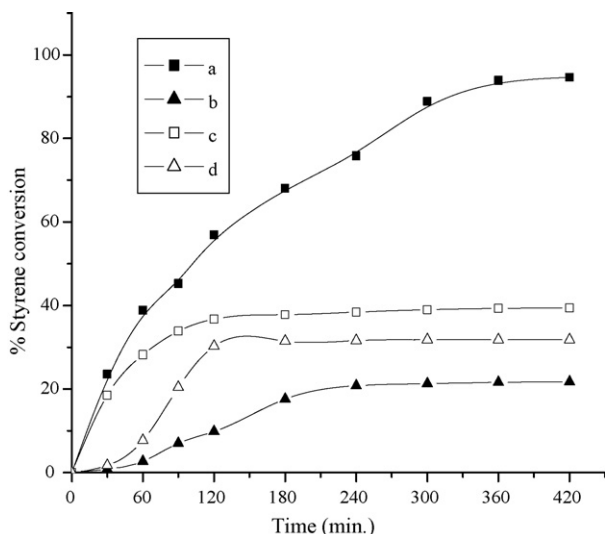
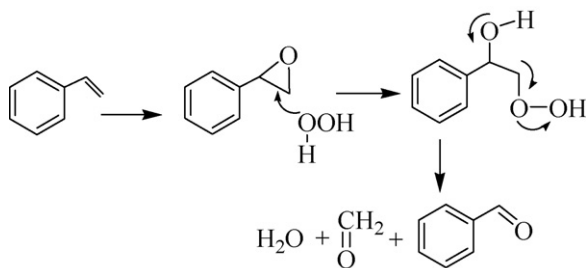


Fig. 9. Catalytic comparison of catalysts for the oxidation of styrene: [VO(sal-dach)]-Y (a), [Cu(sal-dach)]-Y (b), [VO(sal-dach)] (c) and [Cu(sal-dach)] (d).



Scheme 4.

A highest yield of benzaldehyde is possibly due to further oxidation of styreneoxide formed in the first step by a nucleophilic attack of H₂O₂ on styrene oxide followed by cleavage of the intermediate hydroperoxystyrene; Scheme 4 [20]. Similarly, the formation of phenylacetaldehyde is possible through the isomerisation of styreneoxide. The presence of styreneoxide in low percentage is thus likely. The formation of benzalde-

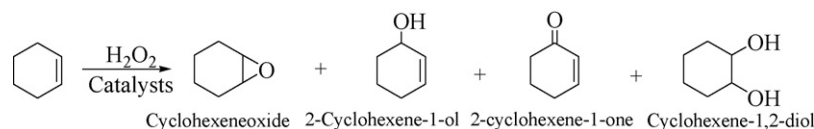
hyde may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via a radical mechanism. High amount of water present in H₂O₂ is partly responsible for the possible hydrolysis of styreneoxide to 1-phenylethane-1,2-diol. Other products e.g. benzoic acid formation is possible due to further oxidation of benzaldehyde.

Catalytic potential of these complexes cannot be compared directly with similar complexes due to limited literature. About 34.8% conversion of styrene was noted with zeolite-Y encapsulated [VO(salphen)] using 70% *tert*-butylhydroperoxide as an oxidant [19]. 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 [18]. 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) [22].

3.2.2. Oxidation of cyclohexene

Complexes [VO(sal-dach)]-Y and [Cu(sal-dach)]-Y catalyze the oxidation of cyclohexene by H₂O₂ efficiently to give cyclohexeneoxide, 2-cyclohexene-1-ol, cyclohexane-1,2-diol and 2-cyclohexene-1-one as presented in Scheme 5. Reaction conditions have also been optimized for the maximum oxidation of cyclohexene by varying different parameters.

Three different cyclohexene:H₂O₂ molar ratios viz. 1:1, 1:2 and 1:3 were considered while keeping the fixed amount of cyclohexene (0.82 g, 10 mmol) and catalyst (0.025 g) in 20 ml of MeCN and reaction was carried out at 75 °C. The percentage conversions noted at various times are presented in Fig. 10. A maximum of 52.8% conversion was noted for the cyclohexene to H₂O₂ ratio of 1:1 in 6 h of reaction time. This conversion reached to 68.3% at a cyclohexene to H₂O₂ molar ratio of 1:2. Increasing cyclohexene:H₂O₂ ratio further to 1:3 results in only 48.0% conversion of cyclohexene. This is possibly due to the presence of excess water as has been noted earlier also. Thus, a large amount of oxidant is not an essential condition to maximize the oxidation.



Scheme 5.

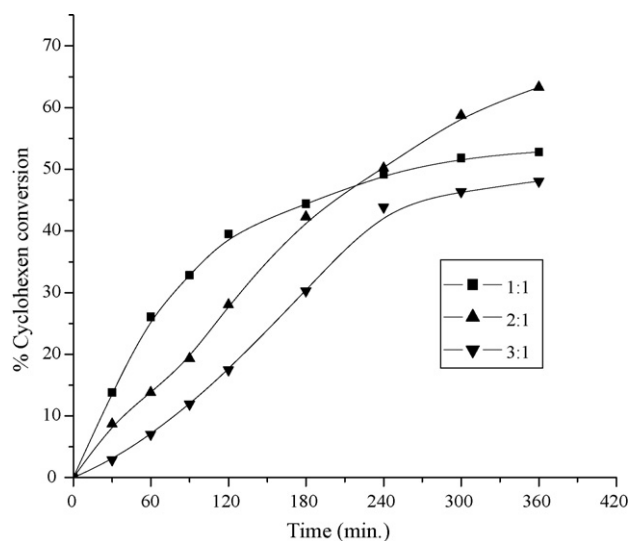


Fig. 10. Effect of H_2O_2 concentration on the oxidation of cyclohexene.

The effect of amount of catalyst on the oxidation of cyclohexene is shown in Fig. 11. Three different amounts of catalyst viz. 0.015, 0.025 and 0.035 g were considered while keeping other conditions as above. It is clear from the plot that 0.035 g catalyst amount is the best one to obtain the highest (86.6%) cyclohexene conversion. Temperature also has influenced the oxidation of cyclohexene. As shown in Fig. 12, amongst three temperatures of 55, 65 and 75 °C, a maximum of 86.6% conversion of cyclohexene was obtained at 75 °C. Thus, optimized conditions for the oxidation of 10 mmol of cyclohexene were fixed as follow: 0.035 g catalyst, 20 mmol 30% aqueous H_2O_2 , 20 ml CH_3CN and 75 °C reaction temperature.

Under the optimized reaction conditions catalyst $[\text{Cu}(\text{sal-dach})]\text{-Y}$ has shown only 18.1% conversion suggesting its poor catalytic ability. The oxidation products identified with this catalyst were cyclohexeneoxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one while one more product cyclohexane-1,2-diol was noted in case of $[\text{VO}(\text{sal-dach})]$. Fig. 13 presents the conversion details as a function of time while

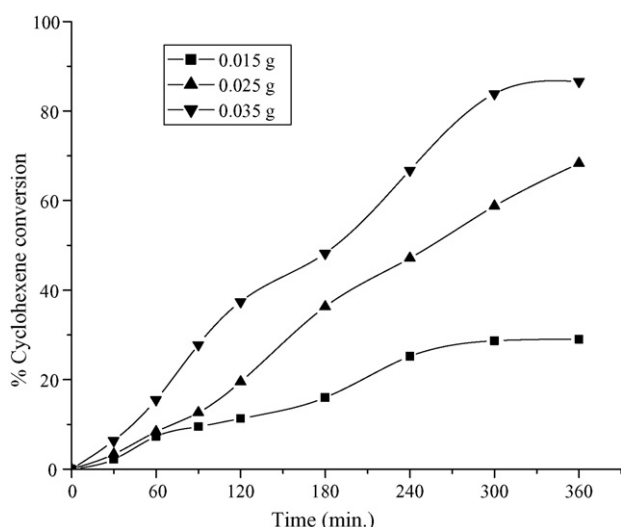


Fig. 11. Effect of amount of catalyst on the oxidation of cyclohexene.

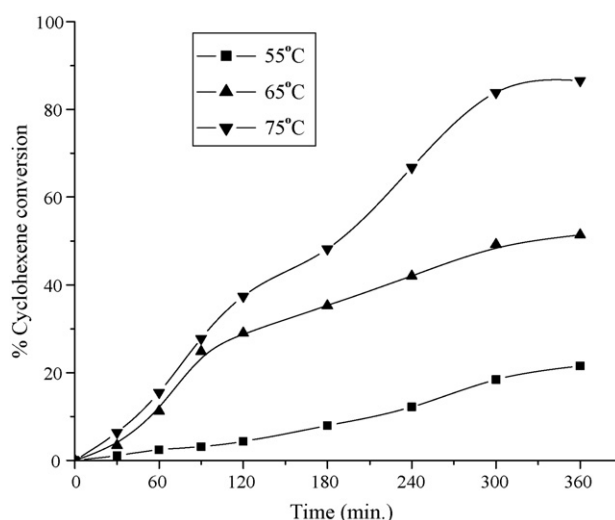


Fig. 12. Effect of temperature on the oxidation of cyclohexene.

Table 5 lists products selectivity along with the conversion and turn over frequency for these catalysts. The selectivity order for the catalyst $[\text{VO}(\text{sal-dach})]$ is: 2-cyclohexene-1-one (53.1%) > 2-cyclohexene-1-ol (27.9%) > cyclohexane-1,2-diol (10.4%) > cyclohexeneoxide (5.0%) and for $[\text{Cu}(\text{sal-dach})]$ is: 2-cyclohexene-1-ol (49.2%) > 2-cyclohexene-1-one (32.0%) > cyclohexeneoxide (18.8%). Thus, in terms of the selectivity of cyclohexeneoxide, $[\text{Cu}(\text{sal-dach})]\text{-Y}$ is better than $[\text{VO}(\text{sal-dach})]\text{-Y}$ (18.8% versus 5.0%), though formation of cyclohexeneoxide is not very encouraging in both cases.

Catalytic activities of these complexes have been compared only with similar complexes. Thus, polymer supported catalysts $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}_n]$ ($[-\text{CH}_2(\text{H}_2\text{sal-dach})_n]$ = polymeric ligand derived from 5,5'-methylenebis(salicylaldehyde) and 1,2-diaminocyclohexane) and $[-\text{S}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}_n]$ ($[-\text{S}_2(\text{H}_2\text{sal-dach})_n]$ = 5,5'-dithiobis(salicylaldehyde) and 1,2-diaminocyclohexane) with very similar ligands exhibit 98% conversion of cyclohexene

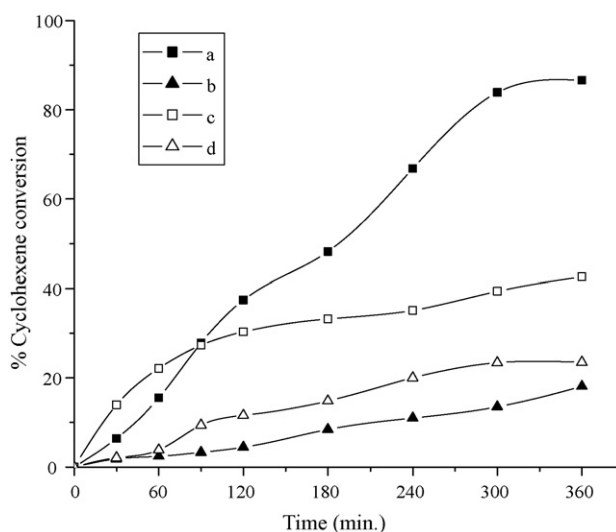






Fig. 13. Effect of catalysts, $[\text{VO}(\text{sal-dach})]\text{-Y}$ (a), $[\text{Cu}(\text{sal-dach})]\text{-Y}$ (b), $[\text{VO}(\text{sal-dach})]$ (c) and $[\text{Cu}(\text{sal-dach})]$ (d) on the oxidation of cyclohexene.

Table 4
Effect of different catalyst on the oxidation of cyclohexene and product selectivity

Catalyst	Conversion (%)	TOF (h ⁻¹)	Product selectivity (%)				
							Others
[VO(sal-dach)]-Y	86.6	249.9	5.0	27.9	53.1	10.4	3.5
[Cu(sal-dach)]-Y	18.1	21.0	18.8	49.2	32.0	–	–
[VO(sal-dach)]	42.6	7.8	7.7	34.4	44.2	5.3	8.4
[Cu(sal-dach)]	23.5	4.3	10.9	45.7	39.4	2.2	1.8

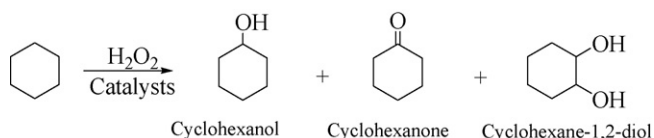
using *tert*-butylhydroperoxide as an oxidant and are much better than both the catalysts reported here [24].

Neat complexes [VO(sal-dach)] and [Cu(sal-dach)] exhibit 42.6 and 23.5% conversion, respectively, and thus have good catalytic activity. The order of the selectivity of reaction products is also same as observed for their encapsulated analogues. Again, the formation of cyclohexeneoxide in both cases is extremely low. Table 4 presents data for neat as well as encapsulated complexes. The calculated turn over frequency in both cases is low (7.8 for [VO(sal-dach)] and 4.3 for [Cu(sal-dach)]) as compared to encapsulated complexes (249.9 for [VO(sal-dach)] and 21.0 for [Cu(sal-dach)]). Thus, turn over frequency as well as other characteristics, such as, stability, recycle ability and operational flexibility make the encapsulated catalysts better over neat complexes.

3.2.3. Oxidation of cyclohexane

We have also carried out the oxidation of cyclohexane under the operating conditions optimized for cyclohexene. Thus, 20 mmol 30% H₂O₂, 0.035 g catalyst and 20 ml CH₃CN were considered for 10 mmol of cyclohexane and reaction was carried out at 70 °C. Under these reaction conditions, catalysts [Cu(sal-dach)]-Y and [VO(sal-dach)]-Y gave 78.1 and 21.0% conversion, respectively, of cyclohexane with major reaction products of cyclohexanone, cyclohexanol and cyclohexane-1,2-diol as shown in Scheme 6. About 2 h was required to achieve equilibrium in these reactions. Amongst the various products formed, the selectivity of cyclohexanol was found to be highest (82.2% for [Cu(sal-dach)]-Y and 93.3% for [VO(sal-dach)]-Y) while selectivities of other two products were much less. Neat complexes have also shown relatively good catalytic activity. However, the TOF values, as noted in other cases, are high and are 190 (for [Cu(sal-dach)]-Y) and 127.2 (for [VO(sal-dach)]-Y). All these details are presented in Table 5.

Catalytic potential of these complexes has been compared indirectly due to limited literature. Neat [Cu(salen)] exhibits only 18% conversion of cyclohexene [16]. Other catalysts have shown comparable catalytic activities [25].



Scheme 6.

3.2.4. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the methanolic solution of neat complexes was treated with 30% H₂O₂ dissolved in methanol and the progress of the reaction was monitored by electronic absorption spectroscopy. Thus, the titration of ca. 10⁻⁴ M methanolic solution of [VO(sal-dach)] with one-drop portions of 30% H₂O₂ dissolved in methanol resulted in decrease in the band maximum at 360 nm, while the intensity of UV band at 277 nm slowly increases with marginal shift and appears as a broad band; Fig. 14. The weak broad band appearing at 568 nm slowly decreases its intensity and finally disappears (see inset of Fig. 14). All these suggest the interaction of H₂O₂ with oxovanadium(IV) centre to give oxoperoxovanadium(V) species. Similar results have also been noted earlier when [VO(sal-dach)] was titrated with *tert*-butylhydroperoxide [24]. Such peroxy species is responsible for the transfer of oxygen atom to the substrates. However, no change in the IR as well as electronic spectral features of the recovered encapsulated complex after first cycle of all catalytic reactions and drying after washing with acetonitrile suggest that the oxidized species acquires its original state and exists as [VO(sal-dach)].

Similarly, the titration of ca. 10⁻⁴ mol methanolic solution of [Cu(sal-dach)] with one-drop portions of 30% H₂O₂ dissolved in methanol resulted in decrease in the band maximum at 561 nm without changing its position. At the same time the band

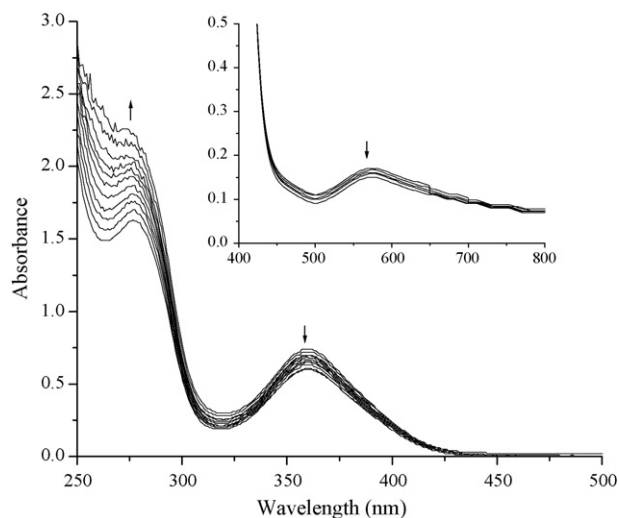


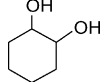


Fig. 14. Titration of [VO(sal-dach)] with 30% H₂O₂. The spectra were recorded after successive addition of one drop portions of H₂O₂ to 10 ml of ca. 10⁻⁴ M solution of [VO(sal-dach)] in methanol.

Table 5
Effect of different catalysts on the oxidation of cyclohexane and product selectivity

Catalyst	Conversion (%)	TOF (h ⁻¹)	Product selectivity (%)			
						Others
[VO(sal-dach)]-Y	78.1	190.0	4.8	82.2	8.7	4.3
[Cu(sal-dach)]-Y	21.0	127.2	2.0	91.2	4.7	2.1
[VO(sal-dach)]	36.8	14.1	2.4	93.1	3.2	1.3
[Cu(sal-dach)]	40.9	15.8	1.8	90.3	1.5	6.4

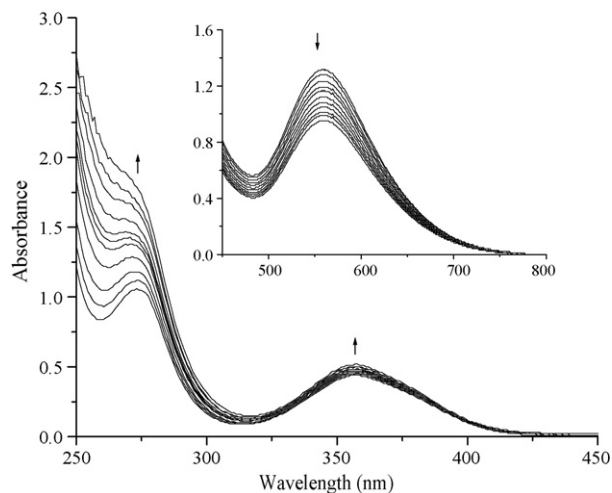


Fig. 15. Titration of [Cu(sal-dach)] with H₂O₂. The spectra were recorded after successive addition of one drop portions of H₂O₂ to 10 ml of ca. 10⁻⁴ M solution of [Cu(sal-dach)] in methanol.

at 357 nm experiences only slight increase in intensity while 273 nm band gradually shifts to 266 nm along with the increase in band maximum and finally disappears. Fig. 15 presents all these spectral changes observed. Again, these changes suggest the interaction of H₂O₂ with Cu(II) centre.

At least three types of intermediates having copper-oxygen interaction viz. side-on Cu^{III}-(μ-η²-peroxo)-Cu^{III}, bis(μ-oxo)-Cu^{III} and Cu^{III}-O-O-H (copper-hydroperoxide) have been reported in the literature during catalytic action [26]. A monomeric copper-hydroperoxide species formation may be expected in the zeolite encapsulated copper(II) complex. Hydroperoxocopper complexes are known to exhibit a charge transfer band at ca. 600 nm [27]. The decrease in intensity of 561 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. Such in situ generated intermediate species finally transfers coordinated oxygen atoms to the substrates to give products. Thus, the catalytic performance of encapsulated catalyst could be attributed to the formation of facile and reversible intermediate species.

4. Conclusions

Complexes [VO(sal-dach)] and [Cu(sal-dach)] have been encapsulated in the super cages of zeolite-Y and their encapsulation has been ensured by different studies. These complexes

have potential catalytic activities for the oxidation of styrene, cyclohexene and cyclohexane. Reaction conditions have been optimized considering different parameters to get maximum conversion of these substrates. A maximum of 94.6% conversion has been obtained with [VO(sal-dach)]-Y. The selectivity of these products follows the order: benzaldehyde (54.5%) > 1-phenylethane-1,2-diol (22.5%) > benzoic acid (8.9%) > styrene oxide (7.6%) > phenyl acetaldehyde (4.9%). With four products having selectivity order: benzaldehyde (69.0%) > styreneoxide (12.9%) > phenyl acetaldehyde (12.0%) > benzoic acid (7.1%), [Cu(sal-dach)]-Y gave only 12.7% conversion. With 86.6% conversion of cyclohexene for [VO(sal-dach)]-Y, the selectivity of four different products follow the order: 2-cyclohexene-1-one (53.1%) > 2-cyclohexene-1-ol (27.9%) > cyclohexane-1,2-diol (10.4%) > cyclohexeneoxide (5.0%). [Cu(sal-dach)]-Y gave only 18.1% conversion and only three products have been obtained with the following order of selectivity: 2-cyclohexene-1-ol (49.2%) > 2-cyclohexene-1-one (32.0%) > cyclohexeneoxide (18.8%). This order of catalytic activity is reverse during the oxidation of cyclohexane. A maximum of 78.1% of cyclohexane with [Cu(sal-dach)]-Y and only 21.0% with [VO(sal-dach)]-Y has been obtained where selectivity of three major products follows the order: cyclohexanol > cyclohexane-1,2-diol > cyclohexanone. Generally vanadium based catalyst is more active than copper based catalyst which is interpreted due to the readily formation of peroxo complex and transferring the oxygen to the substrates. These complexes are stable and do not leach during the catalytic reaction as has been confirmed by testing the filtrate for the corresponding metal ion and thus suggest their heterogeneous nature. The high turn over frequencies of the complexes make them suitable catalysts for these catalytic oxidations.

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