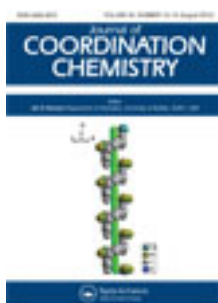


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## Oxidation of styrene and cyclohexene with TBHP catalyzed by copper(II) complex encapsulated in zeolite-Y

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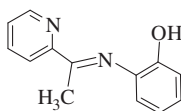
Reaction of monobasic tridentate Hacpy-oap (Hacpy-oap = Schiff base derived from 2-acetylpyridine and *o*-aminophenol) with  $\text{Cu}^{\text{II}}\text{Cl}_2$  in refluxing methanol results in formation of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$ . DFT calculations have been used to optimize structure of the complex.  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  has also been encapsulated in the nanocavity of zeolite-Y and its encapsulation ensured by various physico-chemical techniques. Neat as well as encapsulated complexes are active catalysts for oxidation of styrene and cyclohexene using *tert*-butylhydroperoxide. Reaction conditions for oxidation of these substrates have been optimized by concentration of oxidant, amount of catalyst, volume of solvent and temperature of the reaction mixture.  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  does not leach metal ion during catalytic activity and is recyclable.

**Keywords:** Zeolite-Y;  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$ ;  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$ -Y; Catalyst; Oxidation of cyclohexene; Oxidation of styrene

### 1. Introduction

Catalytic properties of transition metal complexes are controlled by metal and their electronic and structural properties [1, 2]. Oxygen transformations catalyzed by transition metal complexes to produce more valuable organic compounds, such as alcohols, aldehydes, and ketones, require selective oxidation of strong C–H bonds. In homogeneous systems the catalytic activity of the complexes slowly decreases with time due to their slow decomposition, dimerization, or formation of oxo- or peroxy-bridged complexes. Heterogenization of homogeneous catalysts has been sought to avoid such complications [3–5]. Zeolite encapsulated metal complexes (ZEMC) hold a key place and are suggested as model compounds for enzyme mimicking [6, 7]. Encapsulations of complexes in the nano-cavity of zeolite-Y is a process that does not require interactions between the catalyst and the support, and thus maintain inherent advantages of homogeneous catalytic systems [4]. Such ZEMC have provided the opportunity to

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Scheme 1. Structure of (Hacpy-oap; I).

develop catalytic processes for selective oxidation of various substrates and produce important intermediates and industrial products [2, 4, 6–11]. Most encapsulated complexes show better activity than their respective non-encapsulated counterparts. In many cases these are more active, easily recyclable and maintain activity after several cycles of catalytic use.

We have encapsulated copper(II) complex of the Schiff base derived from 2-acetylpyridine and *o*-aminophenol (scheme 1) in the super cages of zeolite-Y. Its catalytic potential has been tested for oxidation of styrene and cyclohexene. The oxidation of styrene is of great interest because styrene oxide and benzaldehyde are important and versatile synthetic intermediates in chemical industry [12, 13]. Selective oxidation of styrene has been reported using various homogeneous catalysts, e.g., metal complexes [14–17] and supported heterogeneous catalysts such as mixed metal oxides [18], zeolites [19], ZEMC [20], metal complexes supported on mesoporous materials [21, 22], etc. Copper complexes encapsulated in the cavity of zeolite-Y have been used as catalyst for oxidation of cyclohexene where various oxidation products such as cyclohexene oxide, 2-cyclohexene-1-one, 2-cyclohexene-1-ol, cyclohexane-1,2-diol, etc. have been identified [23–27].

## 2. Experimental

### 2.1. Materials and methods

Copper(II) nitrate (Qualigens, India), 2-acetylpyridine, *o*-aminophenol, cyclohexene (Himedia, India), styrene (Acros Organics, USA), 70% (w/v) *tert*-butylhydroperoxide (TBHP) (E. Merck, India) were used as obtained. Y-zeolite (Si/Al = 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. Copper exchanged zeolite-Y [Cu<sup>II</sup>-Y] was prepared as reported previously [28]. Found: Cu (ICP-MS), 7.6%. All other chemicals and solvents used were of AR grade.

Elemental analyses of the ligand and complex were obtained by an Elementar model Vario-EL-III. Electronic spectrum of encapsulated complex was recorded in Nujol using a Shimadzu 1601 UV-Vis spectrophotometer by layering the mull of the sample inside a cuvette while keeping the other one layered with Nujol as reference. Spectra of neat complex and ligand were recorded in methanol. IR spectra were recorded as KBr pellets on a Nicolet NEXUS Aligent 1100 series FT-IR spectrometer after grinding the sample with KBr. Thermogravimetric analysis of the encapsulated complex was carried out using a Perkin Elmer (Pyris Diamond) instrument in air with a heating rate of 10°C min<sup>-1</sup>. Scanning electron micrographs (SEMs) of Na-Y and encapsulated catalyst were recorded on a Leo instrument model 435VP; the samples were dusted on alumina and coated with a thin film of gold to prevent surface charging and to protect the

surface material from thermal damage by the electron beam. In all analyses a uniform thickness of about 0.1 mm was maintained. X-ray powder diffractograms of solid catalyst were recorded using a Bruker AXS D8 Avance X-ray powder diffractometer with a Cu-K $\alpha$  target. A thermoelectron gas-chromatograph with an HP-1 capillary column (HP-1, 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) was used to analyze the reaction products. The identity of the products was confirmed by GC-MS using a Perkin-Elmer Clarus 500.

Full geometry optimization of the complex was carried out using the density functional theory method at the (U)B3LYP level [29]. All elements except Cu were assigned the 6-31G(d) basis set. LanL2DZ with an effective core potential for Cu was used. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and that there are only positive eigenvalues.

## 2.2. Preparations

**2.2.1. Preparation of Hacpy-oap (I).** A filtered solution of *o*-aminophenol (0.504 g, 5 mmol) in methanol (25 mL) was added to a solution of 2-acetylpyridine (0.605 g, 5 mmol) in methanol (25 mL) with stirring and the resulting reaction mixture was refluxed for 4 h. The volume of solvent was reduced to *ca* 20 mL and *in situ* formed light brown ligand was used for further reaction. Yield: 64%. Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O (212.25) (%): C, 73.57; H, 5.70; N, 13.20. Found (%): C, 73.50; H, 5.78; N, 13.16. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>(ppm)): 8.7(b, 1H), 7.7(d, 1H, aromatic), 7.47(m, 2H, aromatic), 7.41(t, 1H, aromatic), 6.82(b, 2H, aromatic), 6.39(s, 2H, aromatic), 1.60(s, 3H, -CH<sub>3</sub>). Signal due to methyl protons could be seen well in CDCl<sub>3</sub>.

**2.2.2. Preparation of [Cu<sup>II</sup>(acpy-oap)Cl] (1).** A solution of I (equivalent to 5 mmol) was prepared as mentioned above in 50 mL of methanol. A filtered solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.852 g, 5 mmol) prepared in 100 mL methanol was added to the above solution and the resulting reaction mixture was stirred at room temperature for 4 h. After reducing the solvent volume to *ca* 20 mL, the flask was kept at ambient temperature overnight where brown mass separated. This was filtered, washed with methanol and dried in vacuum over silica gel. Yield: 56%. Anal. Calcd for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>OCu (310.04) (%): C, 50.32; H, 3.55; N, 9.03; Cl, 11.45. Found (%): C, 50.5; H, 3.4; N, 9.2; Cl, 11.3.

**2.2.3. Preparation of [Cu<sup>II</sup>(acpy-oap)Cl]-Y (2).** A methanolic solution of *o*-aminophenol (1.64 g, 15 mmol) in 15 mL was added to a solution of 2-acetylpyridine (1.82 g, 15 mmol) already dissolved in 25 mL of methanol. The obtained reaction mixture was refluxed for 4 h in an oil bath; 1.0 g of [Cu<sup>II</sup>]-Y was suspended to the solution and the reaction mixture was heated under reflux for 15 h in an oil bath while stirring. The resulting light brown material was filtered, dried and Soxhlet extracted with methanol followed by acetone to remove excess ligand and metal complex on the surface of the zeolite if any. The uncomplexed metal ions in zeolite were removed by treating with aqueous 0.1 mol L<sup>-1</sup> NaCl solution (200 mL) with stirring for 8 h. It was then washed with doubly distilled water until no precipitate of AgCl was observed in the filtrate on

treating with AgNO<sub>3</sub>. Finally it was dried at 120°C to constant weight. Found: Cu (ICP-MS), 2.6%.

### 2.3. Catalytic activity studies

**2.3.1. Oxidation of styrene.** The catalytic oxidation of styrene was carried out in a 50 mL flask fitted with a water-circulated condenser. An aqueous solution of 70% TBHP (2.56 g, 20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 mL of CH<sub>3</sub>CN 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 [Cu<sup>II</sup>(acpy-oap)Cl]-Y (0.035 g). During the reaction, the products were analyzed quantitatively by gas chromatography by withdrawing small aliquots after specific intervals of time. The identities of the products were confirmed by GC-MS.

**2.3.2. Oxidation of cyclohexene.** An aqueous solution of 70% TBHP (2.56 g, 20 mmol), cyclohexene (0.82 g, 10 mmol) and catalyst (0.035 g) were mixed in 20 mL of CH<sub>3</sub>CN and the reaction mixture was heated at 75°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.

## 3. Results and discussion

Reaction between equimolar amounts of Cu<sup>II</sup>Cl<sub>2</sub> and Hacpy-oap (**1**) in dry, refluxing methanol yields the brown [Cu<sup>II</sup>(acpy-oap)Cl] (**1**). The ligand coordinates out as monoanionic (ONN(1-)) form; equation (1).



Encapsulation of [Cu<sup>II</sup>(acpy-oap)Cl] (**1**) in the nanocavity of zeolite-Y involved the interaction of [Cu<sup>II</sup>]-Y with excess Hacpy-oap in methanol where ligand slowly enters into the cavity of zeolite-Y due to its flexible nature and interacts with copper. Soxhlet extraction using methanol/acetone purified the impure complex. The remaining uncomplexed metal ions in zeolite were removed by exchanging with aqueous 0.1 mol L<sup>-1</sup> NaCl solution. As one extra anionic ligand would be required to balance the overall charges on the Cu<sup>II</sup>, Cl<sup>-</sup> of NaCl used during exchanged process fulfills this requirement. The presence of chloride in complex has been confirmed qualitatively. Hence, the formula of the encapsulated Cu<sup>II</sup> complex may also be written as [Cu<sup>II</sup>(acpy-oap)Cl]; the encapsulated complex is abbreviated as [Cu<sup>II</sup>(acpy-oap)Cl]-Y (**2**). As impure sample of **2** was extracted with methanol and acetone, the copper content (2.6%) after encapsulation is only due to the presence of [Cu<sup>II</sup>(acpy-oap)Cl] in the super cages of zeolite-Y. Due to space constraint in the cavity of zeolite-Y, **1** will exist in its monomeric form in the nanocavity. The observed surface area of [Cu<sup>II</sup>]-Y and [Cu<sup>II</sup>(acpy-oap)Cl]-Y are 752 and 510 m<sup>2</sup> g<sup>-1</sup>, respectively. Thus, encapsulation of metal complex in zeolite-Y led to an apparent reduction in the surface area and pore volume. This decrease depends on the amount of incorporated complex as well as its

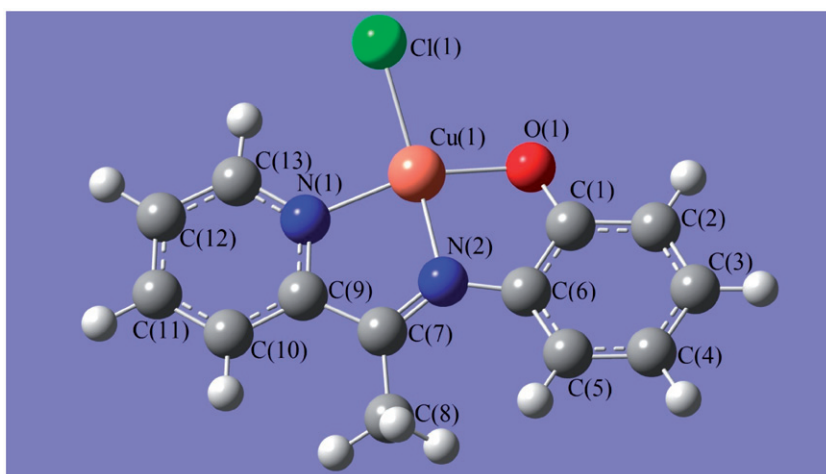


Figure 1. Fully optimized structure of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  (**1**).

Table 1. Selected bond lengths and angles ( $^{\circ}$ ) calculated for  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  compared with literature data.

	Present article	Literature value		
Cu–Cl	2.282	2.248 <sup>b</sup>	N(az)–Cu–Cl <sup>a</sup>	163.465
Cu–N(r) <sup>a</sup>	1.998	2.0511(17) <sup>b</sup> , 1.995(6) <sup>c</sup>	N(r)–Cu–O	159.868
Cu–N(az) <sup>a</sup>	1.997	1.9549(18) <sup>b</sup>	Cl–Cu–O	101.305
Cu–O	1.913	1.9293(15) <sup>b</sup>	N(az)–Cu–O <sup>a</sup>	83.907
			N(az)–Cu–N(r) <sup>a</sup>	81.308
			N(r)–Cu–Cl <sup>a</sup>	96.697

<sup>a</sup>r represents ring nitrogen and az represents azomethine nitrogen.

<sup>b</sup>Ref. [26].

<sup>c</sup>Ref. [30].

molecular size and geometrical conformation inside the zeolitic host. Similarity the spectral properties of neat as well as encapsulated complex (vide infra) suggests a distorted square planar structure for encapsulated complex as well.

### 3.1. DFT studies

The fully optimized DFT structure of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  is presented in figure 1 and computed bond lengths and angles are presented in table 1. The coordination polyhedron around copper, where pyridinic ring nitrogen, enolic oxygen, azomethine nitrogen, and  $\text{Cl}^-$  are involved, is a much distorted square plane. The DFT structural data reveal that Cu–N<sub>ring</sub> bond lengths (1.998 Å), Cu–N<sub>azomethine</sub> (1.997 Å), Cu–O<sub>enolic</sub> (1.913 Å), and Cu–Cl (2.282 Å) are within the values normally found (table 1) for these types of bonds [26, 30]. Similarly, various bond angles around copper compare well with values reported for such complexes. The steric requirements of the molecule,



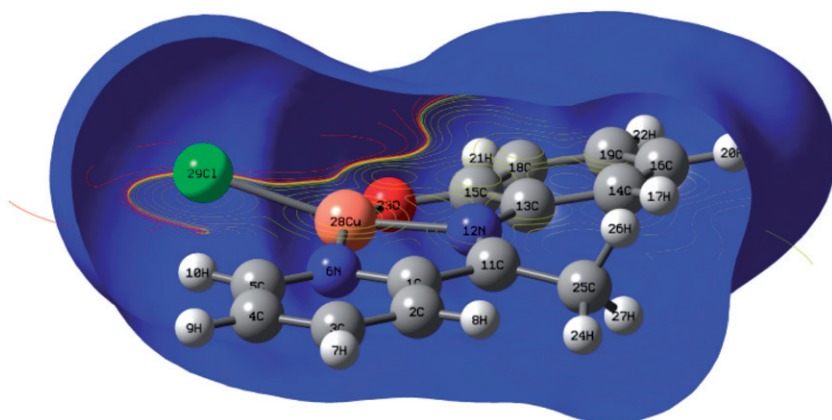


Figure 2. Mapped surface of the total electron density showing the steric requirements of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  (**1**).

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

Compound	IR ( $\text{cm}^{-1}$ ) $\nu(\text{C}=\text{N})$	$\lambda_{\text{max}}$ (nm)
Hacpy-oap ( <b>1</b> )	1587	208, 236, 273, 428
$[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$ ( <b>1</b> )	1633, 1583	228, 235, 268, 435, 500
$[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$ ( <b>2</b> )	1631, 1585	235, 270, 440

considering mapped surface of the total electron density (figure 2), suggests that chloride deviates from the plane containing the four donor atoms. Calculated  $\nu(\text{OH})$  band at  $3670\text{ cm}^{-1}$  in ligand is absent in the complex while the band at  $1652\text{ cm}^{-1}$  in the complex for  $\text{Cu-N}_{\text{ring/azomethine}}$  is close to the observed value ( $1633\text{ cm}^{-1}$ ).

These complexes were further characterized by spectroscopic (IR and UV-Vis) data, elemental analysis, FE-SEM, X-ray powder diffraction pattern, and thermogravimetric analysis.

### 3.2. IR spectral studies

A partial list of IR spectral data is presented in table 2. The intensities of peaks in encapsulated complex are weak due to their low concentration in zeolite matrix, but show similar bands. Comparison of spectra of these catalysts with ligand provides evidence for the coordination mode of the ligand. Ligand exhibits  $\nu(\text{C}=\text{N})$  (azomethine) at  $1640\text{ cm}^{-1}$  and this band moves to lower wavenumbers in complexes ( $1633\text{ cm}^{-1}$  in **1** and  $1631\text{ cm}^{-1}$  in **2**), indicating participation of the azomethine nitrogen in coordination. A weak band at  $ca\ 1585\text{ cm}^{-1}$  is assigned to coordinated pyridine. Absence of band due to hydroxyl group in  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  (**1**) indicates deprotonation followed by coordination of oxygen to copper while presence of such band in  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (**2**) is due to the presence of intra-zeolite water.



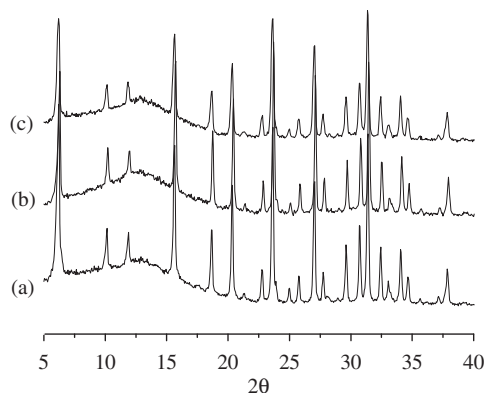


Figure 3. XRD patterns of (a) Na-Y, (b)  $\text{Cu}^{\text{II}}\text{-Y}$ , (c)  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$ .

### 3.3. Electronic spectral studies

Table 2 also presents electronic spectral data of ligand and complexes. The electronic spectrum of the ligand exhibits four bands at 208, 236, 273, and 428 nm. The low energy band (428 nm) is assigned to  $n\text{-}\pi^*$  transition, the bands at 236 and 273 nm are due to split band of  $\pi\text{-}\pi^*$  while 208 nm band is due to  $\varphi\text{-}\varphi^*$  transition. All these bands are also present in  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  (**1**) with slight variations. A broad band at 432 nm is assigned to ligand-to-metal charge transfer (LMCT) from the phenolate oxygen to an empty d orbital of copper. The  $n\text{-}\pi^*$  band merges with this band. In addition, a broad and less intense band at *ca* 500 nm also appears and is assigned to d–d transition, characteristic of copper(II) in a distorted square planar geometry [31, 32]. Encapsulated  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (**2**) displays only bands at 206 and 270 nm in Nujol in the UV region. The d–d transition band could not be located due to poor loading of **1** in the zeolite-Y. However, a LMCT band at 440 nm in the visible region clearly suggests the encapsulation of metal complex.

### 3.4. Powder X-ray diffraction studies

The powder X-ray diffraction patterns of Na-Y,  $[\text{Cu}^{\text{II}}]\text{-Y}$  and encapsulated metal complex  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (**2**) were recorded at  $2\theta$  values between  $5^\circ$  and  $40^\circ$ . The diffraction patterns of encapsulated metal complex,  $[\text{Cu}^{\text{II}}]\text{-Y}$  and Na-Y are similar except a slight change in intensity of the bands in encapsulated complex (figure 3). These observations indicate that the framework of the zeolite has not undergone significant structural change during encapsulation. No new peaks were detected in the zeolite having encapsulated complex due to poor loading of metal complex in the nanocavity of zeolite-Y.

### 3.5. Field-emission-SEM and energy dispersive X-ray analysis studies

Figure 4 presents the field emission SEM of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (**2**) (left) along with the respective energy dispersive X-ray (EDX) analysis plot (right). It is clear from the

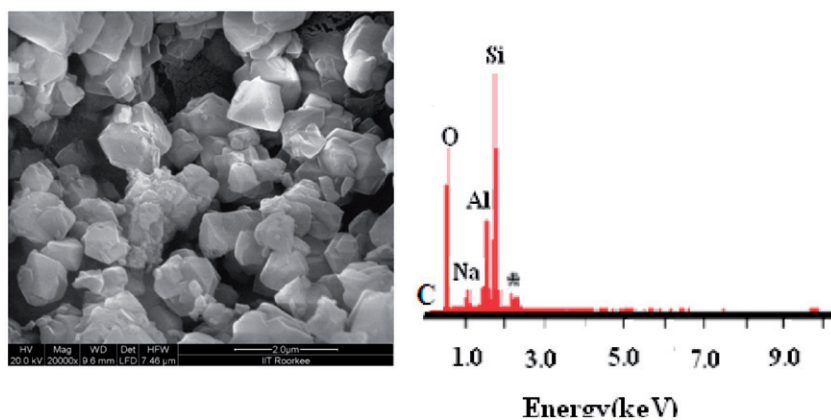


Figure 4. Field emission SEM (Fe-SEM) of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (**2**) (left) along with the respective EDX analysis plot (right).

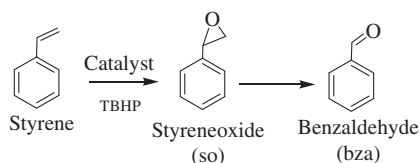
micrograph that copper complex entrapped in zeolite has well-defined crystals and there is no indication of metal ion or complex on the surface. EDX analysis plot supports this conclusion as no copper or nitrogen contents were noted on the spotted surface in the plot. The average silicon and aluminum percentage obtained on the spotted surfaces were *ca* 28% and *ca* 11%, respectively. Sodium, *ca* 3%, suggests the exchange of remaining free copper by sodium during re-exchange process (Experimental section). Only a small amount of carbon (*ca* 4%) and no nitrogen suggest the presence of trace amount of solvent (methanol) from which it was finally washed after Soxhlet extraction. No morphological changes on the surface upon encapsulation of the complexes in the cavity are seen due to their poor loading.

### 3.6. Thermogravimetric analysis

The thermogravimetric analysis data of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (**2**) along with the percent weight loss at different steps and their assignments are presented here. The thermogram of encapsulated complex indicates its decomposition in three steps, though these steps are overlapping. The first step involves removal of trapped water of *ca* 3.8% up to 150°C, while the loss of water of *ca* 9.8% is associated with the structural framework and occurs at 170–350°C. The third step involves the slow but exothermic weight loss of *ca* 19.2% in a wider temperature range (350–800°C) due to decomposition of the chelating ligand.

### 3.7. Catalytic activity studies

**3.7.1. Oxidation of styrene.** The oxidation of styrene, catalyzed by  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$ , was carried out using 70% TBHP as an oxidant to give styrene oxide and benzaldehyde along with only minor amounts of unidentified products, scheme 2. These are common products and have been identified by others as well [7, 9–11].



Scheme 2. Oxidation products of styrene.

In the presence of  $\text{H}_2\text{O}_2$ , further oxidation of styrene oxide to other products has also been reported [33, 34].

In search of reaction conditions to achieve maximum oxidation of styrene, the effect of amount of oxidant (moles of TBHP per mole of styrene), catalyst (amount of catalyst per mole of styrene), and temperature of the reaction were studied.

The effect of TBHP on oxidation of styrene is illustrated in figure 5(a). Three different styrene/TBHP molar ratios of 1 : 1, 1 : 2, and 1 : 3 were considered where the mixture of styrene (1.04 g, 10 mmol), catalyst (0.050 g), and oxidant were taken in 20 mL of  $\text{CH}_3\text{CN}$  and the reaction was carried out at  $80^\circ\text{C}$  (entry nos. 1–3 of table 3). Increasing the styrene/TBHP ratio from 1 : 1 to 1 : 2 increases the conversion from 34.7% to 50.8%. Further increasing the ratio to 1 : 3 brings the conversion down to 47.5%. The reason for this may be due to the dilution of the reaction mixture by the presence of larger amount of water molecules in TBHP solution. It is, therefore, concluded that the 1 : 2 molar ratio is best to obtain the maximum styrene conversion of 50.8% in 7 h reaction time.

Amount of catalyst also affects on the conversion. In order to optimize it, four different amounts of catalyst namely, 0.020, 0.035, 0.050, and 0.075 g were taken for the fixed operating conditions of styrene (1.04 g, 10 mmol) and TBHP (2.56 g, 20 mmol) in 20 mL of  $\text{CH}_3\text{CN}$  at  $80^\circ\text{C}$ . As shown in figure 5(b) (entry nos. 2, 5–7 of table 3), increasing the catalyst amount from 0.020 g to 0.035 g improved the styrene conversion from 36.6% to 60.2%. However, increasing the catalyst amount to 0.050 and 0.075 g did not improve the conversion, thereby suggesting that 0.035 g of catalyst is sufficient to effect maximum conversion. The reason for lower conversion at higher catalyst amount may be due to adsorption/chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact.

Figure 5(c) (entry nos. 5, 7, and 8 of table 3) shows the effect of temperature on the oxidation of styrene while keeping amount of catalyst and styrene/TBHP ratio optimized in 20 mL of  $\text{CH}_3\text{CN}$ . Increasing temperature increases the conversion and running the reaction at  $80^\circ\text{C}$  is the best to obtain 60.2% conversion in 7 h of reaction time.

Thus, for maximum oxidation of 10 mmol of styrene optimized parameters (entry no. 5 of table 3) are:  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (0.035 g), TBHP (2.56 g, 20 mmol),  $\text{CH}_3\text{CN}$  (20 mL) and temperature ( $80^\circ\text{C}$ ).

A maximum of 60.2% conversion of styrene with turnover frequency (TOF) of  $61 \text{ h}^{-1}$  has been obtained under optimized conditions after 7 h of reaction time. The styrene oxide, an important product, is obtained in 78.2% selectivity while benzaldehyde is obtained with only 18.2% selectivity. Other minor products (*ca* 3.6%) could not be identified. Higher selectivity of styrene oxide can be explained from the fact that TBHP

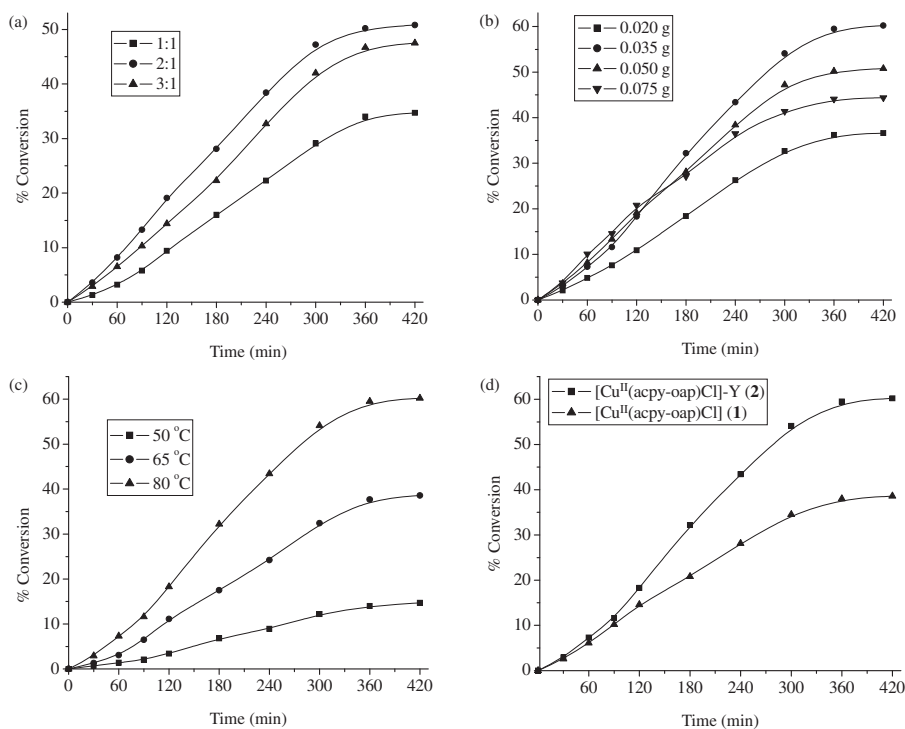
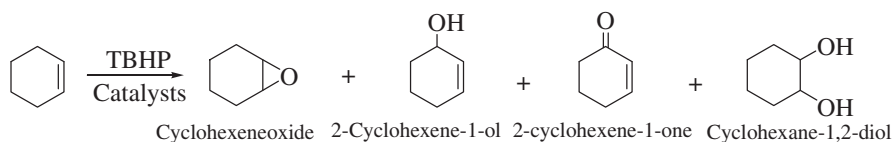


Figure 5. (a) Effect of TBHP concentration (TBHP : styrene) on oxidation of styrene. (b) Effect of amount of catalyst per unit weight of styrene. (c) Effect of temperature on the oxidation of styrene. (d) Effect of different catalysts  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  (1) and  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (2) on oxidation of styrene. See text for reaction conditions of each plot.

Table 3. Conversion of styrene (1.04 g, 10 mmol) using  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  as catalyst in 7 h under different reaction conditions.

Entry No.	Catalyst (g)	TBHP (g, mmol)	Temperature ( $^{\circ}\text{C}$ )	MeCN (mL)	Conv. %
1	0.050	1.28, 10	80	20	34.7
2	0.050	2.56, 20	80	20	50.8
3	0.050	3.84, 30	80	20	47.5
4	0.020	2.56, 20	80	20	36.6
5	0.035	2.56, 20	80	20	60.2
6	0.075	2.56, 20	80	20	44.4
7	0.035	2.56, 20	50	20	14.7
8	0.035	2.56, 20	65	20	38.6

is a milder oxidant leading to the formation of styrene oxide in better yield and does not oxidize further. After washing with acetonitrile and drying, the used catalyst was further used under similar conditions to check its recyclability. About 59.6% conversion of styrene obtained at the end of 7 h with similar selectivity of products suggests its recyclability.



Scheme 3. Oxidation products of cyclohexene.

Neat complex  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  has been used as a catalyst precursor using same mole concentration of copper as in its zeolite encapsulated complex to compare its catalytic activity. Interestingly, this exhibited 38.6% conversion (figure 5d) when complex (0.0028 g, 0.009 mmol), styrene (1.04 g, 10 mmol), TBHP (2.56 g, 20 mmol), and  $\text{CH}_3\text{CN}$  (20 mL) were used and the reaction was carried out at  $80^\circ\text{C}$ . Here, the selectivity of different products is styrene oxide (73.4%) > benzaldehyde (20.7%). Thus, the order is the same as obtained by encapsulated complex and the selectivity of individual products differs only slightly. Blank reaction under above reaction conditions gave 3% conversion. Thus, neat as well as encapsulated complexes are good catalysts. However, the recyclable nature and no leaching of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  makes it better.

Catalytic activity of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  compares well with other catalysts. Metal complex  $[\text{Mn}^{\text{II}}(\text{salen})]$  encapsulated in zeolite-Y exhibits *ca* 30% conversion of styrene using molecular oxygen as an oxidant with excess TBHP as initiator [14]. Zeolite-Y encapsulated  $[\text{V}^{\text{IV}}\text{O}(\text{salphen})]$  exhibits 34.8% conversion of styrene using TBHP as oxidant [15]. Other zeolite encapsulated catalysts such as  $[\text{Mn}^{\text{II}}(3\text{-MeOsalen})]\text{-Y}$  ( $\text{H}_2\text{salen}$  = bis(salicylaldehyde)-1,2-diaminoethane),  $[\text{Mn}^{\text{II}}(3\text{-MeOsalp})]\text{-Y}$  and  $[\text{Mn}^{\text{II}}(\text{salpn})]\text{-Y}$  ( $\text{H}_2\text{salpn}$  = bis(salicylaldehyde)-1,3-diaminopropane) exhibit only 17%, 8.7%, and 7.4% conversions, respectively, using TBHP as oxidant [35]. A maximum of 56.7% conversion of styrene was reported using closely related catalyst  $[\text{Cu}^{\text{II}}(\text{sal-ambmz})\text{Cl}]\text{-Y}$  ( $\text{Hsal-ambmz}$  = Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole) using  $\text{H}_2\text{O}_2$  as oxidant while  $[\text{VO}_2(\text{sal-ambmz})]$  showed much better conversion of *ca* 97% [28].

**3.7.2. Oxidation of cyclohexene.**  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  also catalyzes the oxidation of cyclohexene by 70% TBHP as oxidant to give cyclohexene oxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one, and cyclohexane-1,2-diol as presented in scheme 3. Reaction conditions have also been optimized for cyclohexene.

In order to achieve optimum amount of 70% TBHP for maximum oxidation of cyclohexene, four different cyclohexene to aqueous 70% TBHP molar ratios namely 1 : 1, 1 : 2, and 1 : 3 were considered for a fixed amount of cyclohexene (0.82 g, 10 mmol) and catalyst (0.035 g) in 20 mL of MeCN and reaction was carried out at  $75^\circ\text{C}$ . As illustrated in figure 6(a) (entry nos. 1–3 of table 4), a maximum of 41.1% conversion was achieved in 6 h at a cyclohexene to TBHP molar ratio of 1 : 1. Increasing the ratio to 1 : 2 improved the conversion to 61.3%, while further increasing the ratio to 1 : 3 brings the conversion back to 58.5%.

Under the operating conditions above, i.e. cyclohexene (0.82 g, 10 mmol), TBHP (2.56 g, 20 mmol), MeCN (20 mL) and temperature ( $75^\circ\text{C}$ ), the effect of catalyst using 0.015, 0.025, 0.035, and 0.045 g as a function of time was studied (entry nos. 2, 4–6

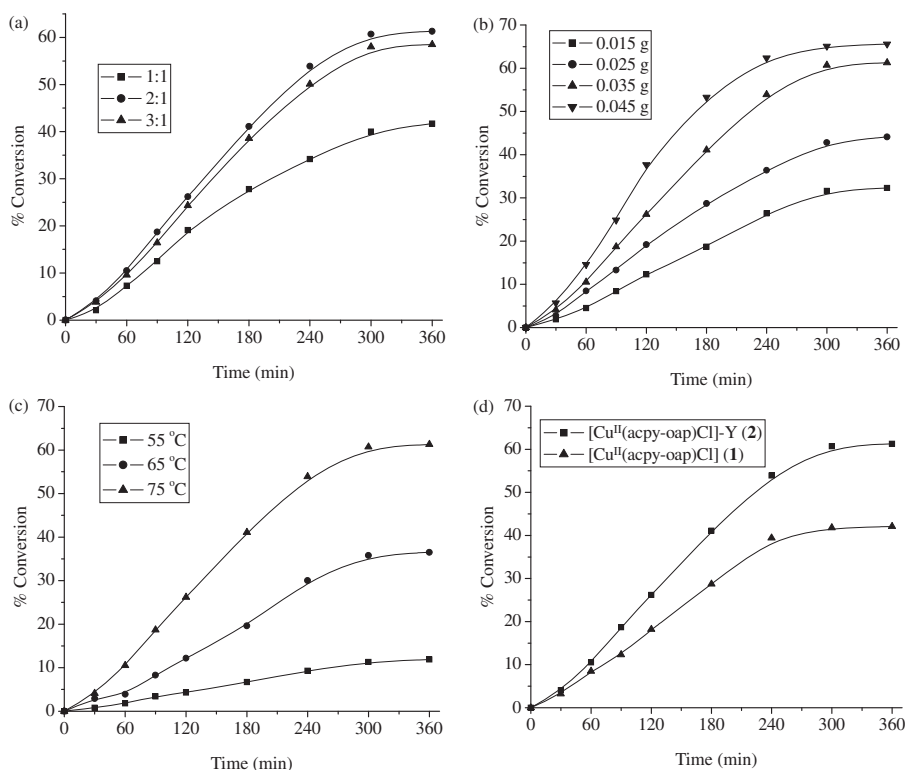


Figure 6. (a) Effect of TBHP concentration (TBHP:cyclohexene) on oxidation of cyclohexene. (b) Effect of amount of catalyst on oxidation of cyclohexene. (c) Effect of reaction temperature on oxidation of cyclohexene. (d) Effect of different catalysts  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  (1) and  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (2) on oxidation of cyclohexene.

Table 4. Conversion of cyclohexene (0.82 g, 10 mmol) using  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  as catalyst in 6 h under different reaction conditions.

Entry No.	Catalyst (g)	TBHP (g, mmol)	Temperature (°C)	MeCN (mL)	Conv. %
1	0.035	1.28, 10	75	20	41.4
2	0.035	2.56, 20	75	20	61.3
3	0.035	3.84, 30	75	20	58.5
4	0.015	2.56, 20	75	20	32.3
5	0.025	2.56, 20	75	20	44.1
6	0.045	2.56, 20	75	20	65.3
7	0.035	2.56, 20	55	20	11.9
8	0.035	2.56, 20	65	20	36.5

of table 4) and results are illustrated in figure 6(b). A maximum of 32.3% oxidative conversion was achieved in 6 h of reaction time with 0.015 g of catalyst. This conversion increases on further increasing the catalyst amount, i.e. 44.1% with 0.025 g, 61.3% with 0.035 g, and 65.6% with 0.045 g. However, 0.035 g of catalyst can be considered the suitable one as increasing the amount increases the conversion as well as turnover rates, only marginally.

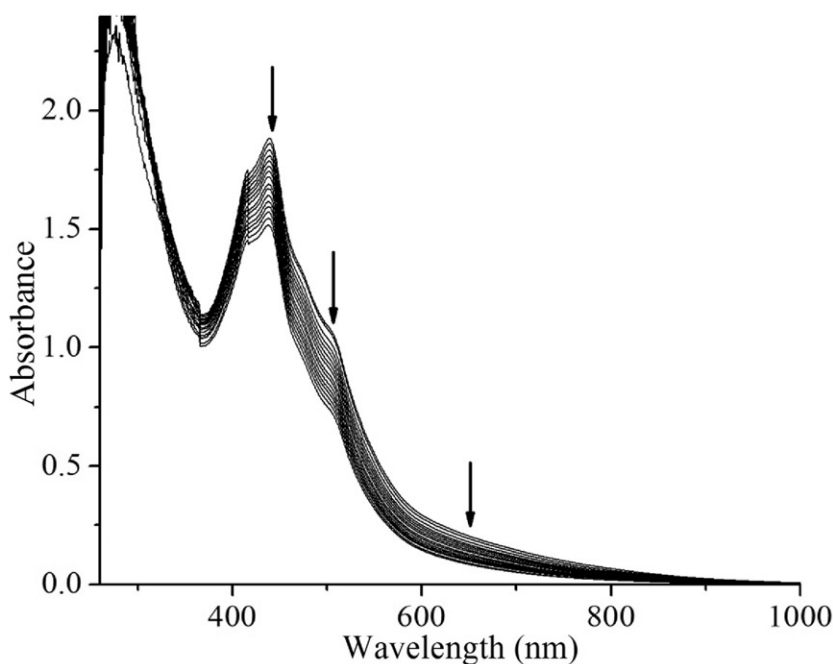


Figure 7. UV-Vis spectral changes observed during titration of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  with TBHP. The spectra were recorded after successive addition of one drop portions of TBHP in minimum methanol to 10 mL of *ca*  $10^{-4} \text{ mol L}^{-1}$  solution of  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  in methanol.

After optimizing the cyclohexene to TBHP molar ratio and catalyst amount, temperature was also varied in the range 55–75°C (entry nos. 2, 7, and 8 of table 4) while keeping other parameters as optimized above. It is evident from figure 6(c) that increasing the temperatures increases the conversion and 75°C is the best to obtain 61.3% conversion in 6 h of reaction time.

Thus, for the maximum oxidation of 10 mmol of cyclohexene optimized parameters are:  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]\text{-Y}$  (0.035 g), TBHP (2.56 g, 20 mmol),  $\text{CH}_3\text{CN}$  (20 mL) and temperature (75°C). Under the optimized reaction conditions, a maximum of 61.3% conversion of cyclohexene with TOF of  $72 \text{ h}^{-1}$  was obtained in 6 h of reaction time. At 6 h, the selectivity of different products is cyclohexane-1,2-diol (77.7%) > 2-cyclohexene-1-ol (11.1%) > cyclohexene epoxide (4.7%) > 2-cyclohexene-1-one (4.6%). After washing with acetonitrile and drying, the used catalyst was further used under similar conditions. About 60% conversion of cyclohexene was obtained at the end of 6 h while maintaining the selectivity of reaction products. A maximum of 42.1% conversion of cyclohexene was obtained with neat catalyst precursor  $[\text{Cu}^{\text{II}}(\text{acpy-oap})\text{Cl}]$  under similar conditions (Figure 6d) where product selectivity varied in the order: cyclohexane-1,2-diol (73.5%) > 2-cyclohexene-1-ol (9.2%) > cyclohexene epoxide (6.8%) > 2-cyclohexene-1-one (3.4%). Thus, neat complex also maintains the selectivity obtained for the encapsulated complex, though conversion is relatively lower.

Catalytic potential of the encapsulated complex presented here compares well with similar encapsulated complexes. For example,  $[\text{Cu}(2\text{-pyrazinecarboxylate})_2]\text{-Y}$  exhibited as high as 90.5% conversion of cyclohexene at a substrate to oxidant (30%  $\text{H}_2\text{O}_2$ ) ratio



of 1 : 2 where no formation of cyclohexene epoxide was observed and selectivity of the other oxidation products varied, 2-cyclohexene-1-one (51%) > 2-cyclohexene-1-ol (42.4%) > cyclohexane-1,2-diol (6.6%) [24]. [Cu(sal-oaba)(H<sub>2</sub>O)]-Y, however, exhibited only 45.8% conversion with the formation of only 2-cyclohexene-1-one and 2-cyclohexene-1-ol [23]. Cyclohexene was oxidized very slowly by TBHP using [Cu(pan)Cl]-Y (where Hpan = 1-(2-pyridylazo)-2-naphthol) under aerobic conditions and only 28% conversion was obtained. Here, the percent selectivity of products varied, 1-*tert*-butylperoxy-2-cyclohexene 89% > 2-cyclohexene-1-one (11%) [25]. Under optimized conditions nearly quantitative oxidation (99.6%) of cyclohexene with [Cu(hap-inh)Cl]-Y was achieved using H<sub>2</sub>O<sub>2</sub> as oxidant where the selectivity of different products followed the order, 2-cyclohexene-1-ol (44%) > 2-cyclohexene-1-one (40%) > cyclohexene epoxide (12%) > cyclohexane-1, 2-diol (4%) [26].

### 3.8. Possible reaction mechanism

To propose a mechanism for the catalytic reaction, we studied the interaction of [Cu<sup>II</sup>(acpy-oap)Cl] (1) with TBHP. Addition of one drop portions of TBHP in minimum amount of methanol to 10 mL of *ca* 10<sup>-4</sup> mol L<sup>-1</sup> solution of [Cu<sup>II</sup>(acpy-oap)Cl] in methanol results in slow reduction of intensity of the d-d band at 500 nm without changing its position (figure 7). The charge transfer band at 435 nm also experienced decrease in intensity, while the bands at 268, 235, and 228 nm (last two bands not shown in figure) slowly gain intensity and finally disappear. All these suggest the interaction of TBHP with Cu(II) center.

At least three types of intermediates having copper-oxygen interaction namely side-on Cu<sup>III</sup>-( $\mu$ - $\eta^2$ -peroxo)-Cu<sup>III</sup>, bis( $\mu$ -oxo-Cu<sup>III</sup>) and Cu<sup>III</sup>-O-O-H (copper-hydroperoxide) have been discussed in the literature during catalytic action [36, 37]. As [Cu<sup>II</sup>(acpy-oap)Cl] exists monomeric in the cavity of zeolite-Y due to space constraints, facile formation of [(HOO)-Cu<sup>III</sup>(acpy-oap)Cl] is expected in the cavity due to the vacant site on copper complex. A decrease in the intensities of d-d and charge transfer bands along with major changes in UV bands may be due to formation of hydroperoxide [(HOO)-Cu<sup>III</sup>(acpy-oap)Cl] intermediate of the neat complex. Similar observations have also been noted earlier for [Cu<sup>II</sup>(hap-inh)Cl]-Y [26] and [Cu<sup>II</sup>(sal-aebmz)Cl] [28]. Hydroperoxocopper complexes exhibit a charge transfer band at *ca* 600 nm [38]. The decrease in intensity of *ca* 500 nm band without any isosbestic point in neat complex may be due to merging of this additional charge transfer band with the d-d transition. The intermediate finally transfers coordinated oxygen atoms to the substrates to give the products. Thus, catalytic performance of encapsulated catalyst could be attributed to formation of facile and reversible intermediate species.

## 4. Conclusions

Hacpy-oap, an ONN donor, has been used to prepare [Cu<sup>II</sup>(acpy-oap)Cl]. Its encapsulation in the super cages of zeolite-Y gave [Cu<sup>II</sup>(acpy-oap)Cl]-Y. Spectroscopic along with chemical and thermal studies confirmed their structures. The encapsulated complex is active for oxidation of styrene and cyclohexene. Oxidation

of styrene gives 60.2% conversion in 7 h with two main products, styrene oxide (78.2%) and benzaldehyde (18.2%). Oxidation of cyclohexene requires 6 h to attain equilibrium with 61.3% conversion and selectivity cyclohexane-1,2-diol (77.7%) > 2-cyclohexene-1-ol (11.1%) > cyclohexene epoxide (4.7%) > 2-cyclohexene-1-one (4.6%). No leaching of metal ion during catalytic reactions, recyclability and heterogeneous nature are advantages of the catalyst. Neat analog [Cu<sup>II</sup>(acpy-oap)Cl] is also active but exhibits less conversion than encapsulated. Oxidation of cyclohexene proceeds through [(HOO)–Cu<sup>III</sup>(acpy-oap)Cl], formation of which has been demonstrated by electronic absorption spectroscopy.

### Supplementary material

Figures having HOMO, LUMO, IR (ligand and complex), and <sup>1</sup>H NMR spectrum of ligand and complex are submitted as supporting materials.

### Acknowledgments

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### References

- [1] E.N. Jacobsen, W. Zhang, M. Guler. *J. Am. Chem. Soc.*, **113**, 6703 (1991).
- [2] M.S. Niasari. *Microporous Mesoporous Mater.*, **92**, 173 (2006).
- [3] M.R. Maurya, J. Costa Pessoa. *J. Organomet. Chem.*, **696**, 244 (2011).
- [4] M.R. Maurya, A. Kumar, J. Costa Pessoa. *Coord. Chem. Rev.*, **255**, 2315 (2011).
- [5] K.C. Gupta, A.K. Sutar, C.-C. Lin. *Coord. Chem. Rev.*, **253**, 1926 (2009).
- [6] P.P. Knops-Gerrits, D. De Vos, F. Thibault-Starzyk, P.A. Jacobs. *Nature*, **369**, 543 (1994).
- [7] S.P. Verkey, C. Ratnasamy, P. Ratnasamy. *Microporous Mesoporous Mater.*, **22**, 465 (1998).
- [8] N. Herron. *Inorg. Chem.*, **25**, 4714 (1986).
- [9] G.S. Rafelt, J.H. Clark. *Catal. Today*, **57**, 33 (2000), and references therein.
- [10] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman. *Catal. Today*, **57**, 157 (2000).
- [11] G.J. Hutchings. *Chem. Commun.*, 301 (1999).
- [12] G. Grigoropoulou, J.H. Clark, J.A. Elings. *Green Chem.*, **5**, 1 (2003).
- [13] B.S. Lane, K. Burgess. *Chem. Rev.*, **103**, 2457 (2003).
- [14] W. Zeng, J. Li, S. Qin. *Inorg. Chem. Commun.*, **9**, 10 (2006).
- [15] B.M. Choudary, P.N. Reddy. *J. Mol. Catal. A Chem.*, **103**, L1 (1995).
- [16] S.S. Kurek, P. Michorczyk, A.-M. Balisz. *J. Mol. Catal. A Chem.*, **194**, 237 (2003).
- [17] J.-Y. Liu, X.-F. Li, Y.-Z. Li, W.-B. Chang, A.-J. Huang. *J. Mol. Catal. A Chem.*, **187**, 163 (2002).
- [18] N. Ma, Y. Yue, W. Hua, Z. Gao. *Appl. Catal. A: Gen.*, **251**, 39 (2003).
- [19] L.M. Kustov, A.L. Tarasov, V.I. Bogdan, A.A. Tyrlov, J.W. Fulmer. *Catal. Today*, **61**, 123 (2000).
- [20] T. Joseph, D. Srinivas, C.S. Gopinath, S.B. Halligudi. *Catal. Lett.*, **83**, 209 (2002).
- [21] T. Joseph, S.B. Halligudi. *J. Mol. Catal. A Chem.*, **229**, 241 (2005).
- [22] Y. Luo, J. Lin. *Microporous Mesoporous Mater.*, **86**, 23 (2005).
- [23] M.R. Maurya, A.K. Chandrakar, S. Chand. *J. Mol. Catal. A Chem.*, **274**, 192 (2007).
- [24] P. Chutia, S. Kato, T. Kojima, S. Satokawa. *Polyhedron*, **28**, 370 (2009).
- [25] I. Kuźniarska-Biernacka, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves. *J. Catal.*, **278**, 102 (2011).
- [26] M.R. Maurya, C. Haldar, S. Behl, N. Babu, F. Avecilla. *J. Coord. Chem.*, **64**, 2995 (2011).

- [27] M.R. Maurya, B. Singh, P. Adão, F. Avecilla, J. Costa Pessoa. *Eur. J. Inorg. Chem.*, 5720 (2007).
- [28] M.R. Maurya, A.K. Chandrakar, S. Chand. *J. Mol. Catal. A Chem.*, **263**, 227 (2007).
- [29] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß. *Theor. Chim. Acta*, **77**, 123 (1990).
- [30] C.S. Sarkar, A. Mondal, J. Ribas, M.G.B. Drew, K. Pramanik, K.K. Rajak. *Inorg. Chim. Acta*, **358**, 641 (2005).
- [31] R. Kumar, K. Mahiya, P. Mathur. *Indian J. Chem.*, **50A**, 775 (2011).
- [32] G. Batra, P. Mathur. *Inorg. Chem.*, **31**, 1575 (1992).
- [33] M.R. Maurya, M. Bisht, A. Kumar, M.L. Kuznetsov, F. Avecilla, J. Costa Pessoa. *Dalton Trans.*, **40**, 6968 (2011).
- [34] M.R. Maurya, M. Bisht, F. Avecilla. *J. Mol. Catal. A Chem.*, **344**, 18 (2011).
- [35] M. Silva, C. Freire, B. de Castro, J.L. Figueiredo. *J. Mol. Catal. A Chem.*, **258**, 327 (2006).
- [36] E.I. Solomon, P. Chen, M. Metz, S.-K. Lee, A.E. Palner. *Angew. Chem. Int. Ed.*, **40**, 4570 (2001).
- [37] J.P. Klinman. *Chem. Rev.*, **96**, 2541 (1996).
- [38] K.D. Karlin, J.C. Hayes, Y. Gultneh, R.W. Cruse, J.W. McKown, J.P. Hutchinson, J. Zubieta. *J. Am. Chem. Soc.*, **106**, 2121 (1984).