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# Feature article Zeolite-Y immobilized Metallo-ligand complexes: A novel heterogenous catalysts for selective oxidation



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# ABSTRACT

Transition metal [M = Co(II), Cu(II)] complexes of  $H_2L^1$  and  $H_2L^2$  ligands have been prepared as neat and nanohybrid zeolite-Y immobilized complexes. The various analytical tools such as FTIR, ICP-AES, elemental analysis, UV-vis, Brunauer, Emmett and Teller (BET) surface area analysis, Thermal analysis, scanning electron micrographs, Powder XRD, conductivity, magnetic moment, and AAS were employed for the characterization of the prepared catalysts. Among all catalysts, the [Cu(L<sup>1</sup>)]-Y (heterogeneous) and [Cu(L<sup>1</sup>)] (homogeneous) have offered high activity and selectivity over oxidation of cyclohexene. Moreover, the [Cu(L<sup>1</sup>)] and [Cu(L<sup>1</sup>)]-Y were employed as catalyst over various organic substrates at identical reaction condition. The immobilized catalyst [Cu(L<sup>1</sup>)]-Y is found to be moderate active over oxidation of cyclohexane (75.2%,), benzene (8.21%), phenol (14.5%), styrene (87.5), benzyl alcohol (21.5%), limonene (11.2%),  $\alpha$ -pinene (9.15%), and cyclooctane (76.8%) with high TON values (21942-2054). The mechanistic study using UV-vis and FTIR suggests the participation of active metalperoxo species, which is reinforced by its high catalytic activity over limonene (16.3%) in the absence oxidant.

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# 1. Introduction

The development of the environmentally benign catalyst and the new catalytic pathway has grown much interest of researcher in the current research scenario. Especially, the use of  $H_2O_2$  as an oxidant for oxidation reactions has found many advantages such as it strongly oxidize the substrate, it is quite cheap, and it affords water as a byproduct [1]. The catalytic oxidation of cyclohexene, cyclohexane, benzene, phenol, styrene, benzyl alcohol, limonene,  $\alpha$ -pinene, and cyclooctane usually affords oxyfunctionalized derivatives, which are very essential intermediates in the preparation of fragrances, drugs, food additives, agrochemicals, and in industrial reactions [2–4].

It is most desirable that oxyfunctionalized derivatives could be produced by environmentally benign oxidants like hydrogen peroxide using the ecofriendly and recyclable heterogeneous catalyst. Usually, the mineral acids, transition metals, and neat metal complexes are being used as a traditional catalyst over the oxidation reactions due to their high selectivity and activity towards the anticipated product. But the practical utilization of these catalysts is rather provoking due to its difficulty in the separation and retrieval of catalyst from the reaction medium. On the other hand, the uses of heterogeneous catalyst which are fairly easy to operate under severe conditions, highly stable, usually prepared at comparatively low budgets, and can be simply isolated from the products without tedious experimental work has gained considerable interest over the last few decades.

Nowadays, the researchers are trying to merge the edge of both the homo and heterogeneous systems by immobilization of homogeneous catalyst on or into the polymers, MOFs, hydrotalcites, microporous and the mesoporous materials [5–18]. Out of these dynamic methods, immobilization of metallo-ligand complexes inside the zeolite-Y nanovoids has been found to be proper and pleasant since the metal complex once formed inside the nanovoids of the zeolite-Y, is too bulky to spread out and cannot leach into the liquid-phase during the catalytic study [19-27]. Moreover, these heterogeneous catalysts can be easily salvaged due to their high stability as compared to the corresponding homogeneous counterparts. In connection with our previous work [28], we have prepared the metal  $(Cu^{2+}, Co^{2+})$  complexes of H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup> ligands as neat and zeolite-Y immobilized complexes. Primarily, these prepared catalysts were scrutinized over oxidation of cyclohexene to catch the most active homo and heterogeneous catalysts and then these most active catalysts were further tested over various organic substrates.

# 2. Experimental

#### 2.1. Materials

All chemicals were commercially obtainable (Sigma-Aldrich, Rankem, Hi-media) and were used as received. The zeolite-Y (Si/Al = 5.62) was acquired from Hi-media, India. The compound 5-chloro-2-hydroxyacetophenone, 2-hydroxyacetophenone, ethelenediamine, phenol, R-(+)-limonene, benzene, styrene, benzyl alcohol,  $\alpha$ -Pinene, cyclohexane, cyclohexene, and cyclooctane were purchased from sigma Aldrich Ltd. (India). 30% H<sub>2</sub>O<sub>2</sub>, CuSO<sub>4</sub>·5H<sub>2</sub>O and CoSO<sub>4</sub>·7H<sub>2</sub>O in extra pure form were acquired from Rankem (India).

# 2.2. Physical methods and analysis

The quantitative analysis of Si, Al, Na, Co, and Cu was executed by ICP-AES using a model Perkin Elmer optima 2000 DV. The magnetic

property of the neat complexes was measured by the magnetic susceptibility balance (Johnson Metthey and Sherwood model). BET surface area analysis was measured by a multipoint BET method using Micromeritics, ASAP 2010 surface area analyzer. The powder XRD was executed by Bruker AXS D<sub>8</sub> Advance X-ray powder diffractometer with a CuK $\alpha$  ( $\lambda = 1.54,058$ ) target and movable detector. Scanning electron micrographs (SEMs) of  $[Cu(HL^1)]$ -Y were carried out using SEM instrument (model-JSM-5610LV), JEOL. FTIR (4000–400 cm $^{-1}$ ) of were recorded with KBr on a FTIR-8400S Shimadzu. UV-Vis spectra was recorded on "SHIMADZU" UV-2450 spectrophotometer using a quartz cell of 1 cm<sup>3</sup> optical path in  $10^{-3}$  M methanol, and/or aqueous HF. TG analysis was carried out in air atmosphere in the temperature range 30-700 °C using Shimadzu (TGA-500) Instrument. Atomic absorption spectra was recorded on a PerkinElmer 4100-1319. The products during catalytic oxidation were identified by GC-MS having BP-5 capillary column (30 m  $\times$  0.25 mm  $\times$  0.25 m) 95% silicoxane surface and FID detector.

# 2.3. Syntheisis section

The graphical representation of the ligands and neat complexes is manifested in scheme 1.

#### 2.3.1. Preparation of ligands

Ligands viz.  $H_2L^1$  and  $H_2L^2$  were prepared according to reported method and are well characterized in our previous article [28].

## 2.3.2. Preparation of Co (II) and Cu(II) based neat complexes

A dropwise addition of the aqueous metal salt (2.6 mmoL  $CoSO_4 \cdot 7H_2O$  and/or  $CuSO_4 \cdot 5H_2O$ ) solution to a 25 mL of an ethanolic Schiff bases (2.6 mmoL,  $H_2L^1$ , and/or  $H_2L^2$ ) solution leads to the formation of neat metal complexes. The subsequent mixture was heated at 80 °C in a water bath for 4–5 h. After cooling, the solid product was isolated by vacuum filtration and dried for 3 h at 60 °C.

# 2.3.3. Preparation of metal exchanged M (II)–Y (M = Cu, Co)

A much lower concentrate metal salt solution (0.003 M of  $CoSO_4 \cdot 7H_2O$  and/or  $CuSO_4 \cdot 5H_2O$  in 250 mL deionized water) having a pH range between 4 and 4.5 were stirred at 90 °C for 24 h after the addition of 3.0 g pure zeolite-Y into it. As a result, the slurry was isolated, washed with deionized water to confiscate the excess of metal ions present on the surface of zeolite-Y (confirmed by AAS), and then it was dried for 12 h at 120 °C.

## 2.3.4. Preparation of zeolite-Y immobilized metal complexes

A 0.5 g of activated Co(II)-Y and/or Cu(II)-Y was refluxed for 16 h with stochometrically excess amount of ligand ( $H_2L^1$  or  $H_2L^2$ ). The slurry was isolated and treated for Soxhlet extraction with acetonitrile, methanol, chloroform, acetone and DMF to confiscate vexatious excess ligands and the complexes formed on the external surface of M(II)-Y. Subsequently, the material was moderately stirred with 0.01 M NaCl for 6 h to consent the back-exchange of excess uncordinated Co(II) and/or Cu(II) ions with Na<sup>+</sup> ions. Then it was washed with deionized water to wipe out the chloride ions (confirmed by AgNO<sub>3</sub>) from it and dried for 12 h at 140 °C.

# 2.3.5. Catalytic activity

Liquid phase oxidation reactions were performed in a 25 mL RBF fitted with water condenser. The movement of the reaction was supervised as a function of time by withdrawing a small aliquot after certain



Scheme 1. Graphical presentation of neat complexes and ligands.

time intervals and analyzing them quantitatively by GC–MS. Primarily, an oxidation of cyclohexene was carried out to catch the highly active catalysts (homo and heterogeneous) among all the prepared catalyst at identical reaction condition and then most active catalysts were further tested over oxidation of various organic substrates such as cyclohexane, benzene, phenol, styrene, benzyl alcohol, limonene,  $\alpha$ -pinene, and cyclooctane at identical reaction conditions.

# 3. Results and discussion

# 3.1. Elemental analysis

The elemental analysis data of neat complexes (Table 1) reveal that the formation of chelate complexes took place in 1:1 (M:L) metal (Co, Cu) to the ligand mole ratio. Furthermore, the similarities of finding results with the theoretical values clearly support the formation of nonionic metal complexes in 1:1 (M:L) fashioned through deprotonation of both the phenolic –OH group of ligands, making the coordination entities neutral. The non-ionic nature of neat complexes was further reinforced by its lower molar conductivity values (Table 1) [29]. As presented in Table 2, the metal content (Si, Al%) in each zeolite-Y based materials are different due to the different water content in each catalyst (See TGA), however, the similar Si/Al ratio in zeolite-Y based materials and similar C/N ratio in immobilized complexes compared to their respective neat complexes clearly indicates the absence of dealumination during the modification and the existence of metal complexes inside the zeolite-Y nanovoids, respectively. Moreover, the high M/C ratio in immobilized complexes compared to the respective neat complexes clearly specify the presence of uncoordinated extra Cu(II) and/or Co(II) trapped in zeolite-Y; however, it was treated with 0.01 M NaCl during the preparation of immobilized complexes in order to back-exchange the uncoordinated Cu(II) and/or Co(II) ions by Na<sup>+</sup>. In the immobilized complexes, the lesser amount of metal cations compared to the Cu(II)-Y, Co(II)-Y is may be due to the participation of the metal cations in the formation of transition metal complexes within zeolite-Y, or it may be due to trivial leaching of metal ions during the immobilization procedure.

# 3.2. Brunauer, Emmett, and teller (BET) surface area analysis

The surface textural properties of the pure Na-Y, Co(II)-Y, Cu(II)-Y, and zeolite-Y immobilized complexes are presented in Table 3. The

Table 1

Elemental analysis, molar conductivity, and magnetic moment of neat metal complexes.

						*						
Compound	ind Elemental analysis % found (calculated)						Ratio (%)	Ratio (%) M/C	Yield (%)	M.P (°C)	Molar conductivity <sup>b</sup> (S cm <sup>2</sup> mol <sup>-1</sup> )	µ <sub>eff</sub> (B.M)
	С	Н	Ν	M <sup>a</sup>	0	Cl	C/N					
$[Co(L^1)]$	61.19	5.19	7.92	16.64	9.06	-	7.72	0.27	56.19	>300	2.19	4.30
	(61.20)	(5.14)	(7.93)	(16.68)	(9.06)		(7.71)	0.27				
$[Cu(L^1)]$	61.48	4.96	7.94	17.76	7.86	-	7.74	0.28	95.11	>300	1.30	1.78
	(60.41)	(5.07)	(7.83)	(17.76)	(8.93)		(7.71)	0.28				
$[Co(L^2)]$	50.91	3.92	6.57	14.11	7.64	16.85	7.74	0.27	67.51	>300	2.30	4.40
	(51.21)	(3.82)	(6.64)	(13.96)	(7.58)	(16.79)	(7.71)	0.27				
$[Cu(L^2)]$	50.41	3.64	6.52	14.96	7.87	16.60	7.73	0.29	85.39	>300	1.11	1.74
	(50.66)	(3.78)	(6.56)	(14.89)	(7.50)	(16.61)	(7.72)	0.29				

<sup>a</sup> Respective transition metal Co(II) or Cu(II).

<sup>b</sup> Conductivity of neat metal complex was measured using DMSO as solvent at 30 °C.

Table 2
CP-AES analysis data of zeolite-Y based materials with their probable unit cell formulae.

Compound	ICP-AES	ICP-AES elemental analysis (%)					Percentage ratio			Unit cell formulae
	С	Ν	Na	Ma	Si	Al	Si/Al	M/C	C/N	
Na-Y	-	-	5.07	-	33.46	5.95	5.62	-	-	Na <sub>30</sub> [(AlO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]
Co(II)-Y	-	-	4.46	0.829	33.70	5.99	5.62	-	-	Na <sub>26.2</sub> Co <sub>1.90</sub> [(AlO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]
Cu(II)-Y	-	-	4.25	1.011	32.91	5.85	5.62	-	-	Na <sub>25.6</sub> Cu <sub>2.20</sub> [(AlO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]
[Co(L <sup>1</sup> )]-Y	2.07	0.268	4.61	0.609	33.59	5.97	5.62	0.29	7.72	$Na_{27,2}[Co_{1,40}(L^1)_{1,30}(AlO_2)_{30}(SiO_2)_{162}]$
$[Cu(L^1)]-Y$	1.63	0.211	4.64	0.507	33.03	5.87	5.62	0.31	7.71	Na <sub>27.8</sub> [Cu <sub>1.1</sub> (L <sup>1</sup> ) <sub>1.04</sub> (AlO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]
$[Co(L^2)]-Y$	1.92	0.249	4.60	0.564	33.29	5.92	5.62	0.29	7.71	$Na_{27,4}[Co_{1,31}(L^2)_{1,22}(AlO_2)_{30}(SiO_2)_{162}]$
$[Cu(L^2)]-Y$	1.94	0.251	4.71	0.592	33.91	6.03	5.62	0.30	7.72	$Na_{27.5}[Cu_{1.25}(L^2)_{1.21}(AlO_2)_{30}(SiO_2)_{162}]$
$[Cu(L^1)]-Y^b$	1.75	0.227	4.98	0.544	35.45	6.30	5.62	0.31	7.70	$Na_{27.8}[Cu_{1.1}(L^1)_{1.04}(AlO_2)_{30}(SiO_2)_{162}]$

<sup>a</sup> Respective transition metal Co(II) or Cu(II).

<sup>b</sup> Before ICP-OES analysis, recycled catalyst [Cu(L<sup>1</sup>)]-Y was dehydrated at 300 °C for 2 h.

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Table 3
BET <sup>a</sup> surface analysis of zeolite-Y based materials.

	Compound	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>2</sup> /g)	Langmuir Surface area (m²/g)	Loss in pore volume (%)
Ī	Na-Y	539.0	0.327	861.2	_
	Co(II)-Y	495.6	0.301	794.0	08.0
	Cu(II)-Y	482.9	0.293	771.6	10.4
	$[Co(L^1)]-Y$	386.2	0.228	581.1	30.5
	$[Cu(L^1)]-Y$	407.9	0.207	620.3	36.5
	$[Co(L^2)]-Y$	358.0	0.217	572.1	33.5
	$[Cu(L^2)]-Y$	411.3	0.249	657.1	23.7
	$[Cu(L^1)]-Y^b$	435.3	0.218	651.7	33.4

<sup>a</sup> Before analysis, all samples (except last entry) were de-gasified at 110 °C for 2 h to remove any adsorbed gases.

<sup>b</sup> Before BET analysis, recycled catalyst [Cu(L<sup>1</sup>)]-Y was dehydrated at 300 °C for 2 h.

formation of Co(II) and Cu(II) complex inside the nanovoids of zeolite-Y significantly reduced the pore volume, surface area and Langmuir Surface area of the zeolite-Y immobilized complexes. This favors the existence of Cu(II) and Co(II) complexes inside the nanovoids zeolite-Y and not on the peripheral surface of zeolite-Y framework [31,32]. This type of lowering in surface area and pore volume upon immobilization of metal complexes has also been described previously by some researcher [30–32].

# 3.3. X-ray diffraction (XRD) study

The X-ray diffraction (XRD) patterns of pure Na-Y, Co(II)-Y, Cu(II)-Y, and zeolite-Y immobilized complexes are displayed in Fig. 1. The immobilized complexes demonstrate analogous patterns that can be indexed to zeolite-Y; apart from a slight change in the intensity of the peaks, no new crystalline patterns have appeared. This directs that the crystallinity and morphology of the zeolite-Y are conserved upon immobilization and the complexes are well distributed in the nanovoids of zeolite-Y [33]. The relative peak intensities of the 220, 311 and 331 reflections have been supposed to be allied with the locations of cations. In pure zeolite-Y, Co(II)-Y and Cu(II)-Y, the order of peak intensity is:  $I_{331} \gg I_{220} > I_{311}$ , whereas in the immobilized complexes, the order of peak intensity becomes  $I_{331} \gg I_{311} > I_{220}$ . This difference in the relative intensities of the peaks is may be due to the reallocation of arbitrarily coordinated free cations  $(Cu^{+2}, Co^{+2})$  in the zeolite-Y. This observation supports the successful immobilization of metal complexes within the zeolite-Y nanovoids without any kind of demolition in the framework of zeolite-Y. Besides, the indistinguishable XRD pattern of recycled catalyst [Cu(L<sup>1</sup>)]-Y (Fig. 1h) to that of fresh catalyst evidently support the fact that crystallinity and morphology of zeolite-Y framework is wellmaintained even after the catalytic study.

# 3.4. Scanning electron microscopy (SEM) analysis

The SE Micrograph of immobilized complexes before and after soxhlet extraction is displayed in Fig. 2. As shown in SEM of  $[Cu(L^1)]$ -Y taken prior to the soxhlet extraction, the excess redundant particles such as uncoordinated ligands and metal complexes formed on the peripheral surface of zeolite-Y are observable, whereas no redundant particles can be seen in the SEM of  $[Cu(L^1)]$ -Y taken after the soxhlet extraction, demonstrating the successful removal of the surface redundant particles during soxhlet extraction. The particle boundaries on the peripheral surface of zeolite-Y are distinctive and no new crystalline patterns are appearing in the SEM of  $[Cu(L^1)]$ -Y taken after the soxhlet extraction due to the impeccable distribution of complexes inside the nanovoids of zeolite-Y [30]. Moreover, the absence of metal ion leaching, no color change in reaction medium and catalyst during the catalytic study approves a successful removal of extra redundant particles from the external boundaries of zeolite-Y by soxhlet extraction.



**Fig. 1.** XRD pattern of the (a) Na-Y, (b) Co(II)-Y, (c) Cu(II)-Y, (d)  $[Co(L^1)]-Y$ , (e)  $[Cu(L^1)]-Y$ , (f)  $[Co(L^2)]-Y$ , (g)  $[Cu(L^2)]-Y$  and (h) Recycled and dehydrated  $[Cu(L^1)]-Y$ .

# 3.5. Fourier transform infrared (FTIR) spectroscopy

The ligands  $H_2L^1$  and  $H_2L^2$  mainly show bands nearly at 3400–3300 and 1616 cm<sup>-1</sup> due to  $v_{(0-H)}$  (weak band due to hydrogen bonding) and  $v_{(C=N)}$  present in both ligands, respectively [28]. As displayed in Fig. 3, a shift of  $v_{(C=N)}$  band towards lower wavenumbers (1600-1587 cm<sup>-1</sup>) and the disappearance of the weak  $v_{(O-H)}$  broad band in all the neat complexes (Fig. 3f-1) proposes a coordination of azomethyne nitrogen and phenolic oxygen of ligands to the metal ion, respectively. The coordination of metal ions to the ligand through the "N' and "O" atoms is further reinforced by the appearance of new bands at 570–510 and 460–420 cm<sup>-1</sup> region due to the  $v_{(M-O)}$  and v<sub>(M-N)</sub> modes, respectively [34]. The FTIR spectra of Na-Y, Co(II)-Y, Cu(II)-Y, and zeolite-Y immobilized complexes (Fig. 3a-e and g-i) mainly shows the zeolitic bands at 3700-3300, 1635, 445, 580, 800 and  $1050 \,\mathrm{cm}^{-1}$  due to surface hydroxyl groups, lattice water molecules,  $TO_4$  (T = Si, Al) bending mode, symmetric stretching,  $v_{sym}T-O$  (internal), and antisymmetric vibrations, respectively [35]. No broadenings or shift of these vibrations is spotted upon the immobilization of the complexes inside the zeolite-Y which further provision the fact that the zeolite-Y framework conserves upon immobilization of metal complexes [36,37]. The presence of weaker bands in immobilized complexes within the range of  $1620-1210 \text{ cm}^{-1}$  (the range where zeolite-Y materials does not absorb) not only confirm the formation of metal



Fig. 2. SE micrograph of (a)  $[Cu(L^1)]$ -Y taken before Soxhlet extraction (b)  $[Cu(L^1)]$ -Y taken after Soxhlet extraction.

complexes inside the zeolite-Y *but also* suggest its lower concentration within zeolite-Y.

# 3.6. Electronic spectra and magnetic moments

The electronic spectrum of  $H_2L^1$  and  $H_2L^2$  displayed five (390, 320, 284, 272, and 256 nm) and six bands (401, 332, 287, 277, 263, and 258 nm) respectively. The former two bands in both the ligands are due to  $n \rightarrow \pi^*$  transition occurring in azomethyne group, whereas the remaining bands are due to  $\pi \rightarrow \pi^*$  transition occurring in the phenyl rings of ligands [28]. As displayed in Fig. 4a and c, the neat Co(II) complexes of both ligands exhibited bands at 282–233, 306–307, 384–373 and 869–867 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ , charge transfer (*MLCT*), and <sup>4</sup>A<sub>2</sub> (*F*)  $\rightarrow$  <sup>4</sup>  $T_1(P)$  transition (*d*-*d*), respectively. The presence of *d*-*d* bands nearly at 870 nm and magnetic moment value (Table 1) nearly at 4.3–4.4 B.M of both the Co(II) complexes is a characteristic value of cobalt complex with tetrahedral geometry [38]. The Cu(II) complexes of both ligands (Fig. 4b and d) exhibit bands at 287–223, 306–304, 363–352, and 551–550 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ , charge transfer (*MLCT*), and



**Fig. 3.** FTIR spectra of (a) Na-Y, (b) Co(II)-Y, (c) Cu(II)-Y, (d)  $[Co(L^1)]$ -Y, (e)  $[Cu(L^1)]$ -Y, (f) neat  $[Cu(L^1)]$ , (g) Recycled and dehydrated  $[Cu(L^1)]$ -Y, (h)  $[Co(L^2)]$ -Y, (i)  $[Cu(L^2)]$ -Y, (j)  $[Co(L^1)]$ , (k)  $[Co(L^2)]$ , and (l)  $[Cu(L^2)]$ .

 ${}^{2}A_{1g} \rightarrow {}^{2}B_{1g}$  transition (*d*-*d*), respectively. The lower magnetic moment value (Table 1) at about 1.7 B.M and appearance of *d*-*d* bands at 551– 550 nm is a characteristic value of Cu(II) complexes with square-planar geometry [38,39]. As displayed in the Fig. 4e–k, pure Na-Y, and each modified zeolite-Y have exhibits one intense band at 306 nm and the other very weak band nearly at 345 nm due to the charge transfer transition for oxygen to aluminium atoms of two different Al—O units existing in the host zeolite-Y [40,41]. The electronic spectrum of Cu(II)-Y (Fig. 4g) exhibits extra two bands nearly at 740 and 899 nm, which could be attributed to the octahedral geometry of Cu(II) ion surrounded by oxygen atoms of zeolite-Y, whereas no extra bands are observed (Fig. 4f) in Co(II)–Y. The UV–vis spectrum of both Co(II) immobilized complexes (Fig. 4h and j) displayed about five or six bands at 277–228, 291–288 and 365–346 nm, attributed to  $\pi \rightarrow \pi^*$ ,



**Fig. 4.** Electronic spectrum of the (a)  $[Co(L^1)]$ , (b)  $[Cu(L^1)]$ , (c)  $[Co(L^2)]$ , (d)  $[Cu(L^2)]$ , (e) Na-Y, (f) Co(II)-Y, (g) Cu(II)-Y, (h)  $[Co(L^1)]$ -Y, (i)  $[Cu(L^1)]$ -Y, (j)  $[Co(L^2)]$ -Y, and (k)  $[Cu(L^2)]$ -Y.

 $n \rightarrow \pi^*$ , charge transfer transition (*MLCT*), respectively. The electronic spectrum of both the Cu(II) immobilized (Fig. 4i and k) complex also exhibited about five or six bands 277–250, 293–284 and 330–324 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and charge transfer transition (*MLCT*), respectively. Furthermore, the presence of the very less intense *d*-*d* band in both the immobilized Co(II) complex at 856–851 and at 542–521 nm in both the immobilized Cu(II) complexes, hypsochromic shifted to that of their corresponding neat complexes, is characteristic values of the distorted tetrahedral and square planar geometry around the center metal ion, respectively. This hypsochromic shift in immobilized complexes clearly suggests an extra splitting of the energy levels from the barycenter under the impact of zeolite-Y framework. The details of the peak assignment are given in Table 4.

# 3.7. Thermal analysis

The ligand  $H_2L^1$  and  $H_2L^2$  ligands decompose in two stages. In the first stage, nearly 80.11 and 76.56% of weight loss is detected at 30-300 °C due to a major breakdown in the carbon skeleton of ligands  $H_2L^1$  and  $H_2L^2$ , respectively, In the second stage, both the ligands completely decomposes and form CO, CO<sub>2</sub>, NO, NO<sub>2</sub> gases with weight loss of about 19.89 and 23.44%, respectively [28]. The TG of neat complexes (Fig. 5a-d) reveals no considerable weight loss (only 1-2%) below 160 °C owing to the absence of outer-sphere and/or inner sphere water molecule in neat complexes. Both the neat Cu(II) complex shows only one decomposition stage within the temperature range 161-450 ° C with assessed weight loss of 77.20 (calc. 77.89%) and 79.71% (calc. 81.43%) in  $[Cu(L^1)]$  and  $[Cu(L^2)]$ , respectively, corresponding to the elimination of ligands from complexes and leaving behind a cupric oxide as a residue (21.3-19.1%). Similarly, both the neat Co(II) complexes have shown only one stage weight loss of 52.30 (Calc. 52.03%) and 59.29% (calc. 60.61%) in [Co(L<sup>1</sup>)] and [Co(L<sup>2</sup>)], respectively, within the range of 161–500 °C, which could be ascribed to the breakdown of the complexes and leaving behind cobalt oxide as a residue (44.9-39.1%). As displayed in Fig. 5f-l, the thermal decomposition in Na-Y, Co(II)-Y, Cu(II)-Y and zeolite-Y immobilized complexes mainly occurs only in one stage in the temperature range of 50-400 °C owed to the elimination of the physically and chemisorbed water molecules existing in it. Besides, one more decomposition stage of 2-3% of weight loss is detected in each immobilized complexes (Fig. 5h-l) beyond 400 °C which indicates the existence of the metal complexes in lower concentration within the zeolite-Y nanovoids. The weight loss in immobilized complexes is extended up to 400 °C compared to the respective neat complexes, which indicates that the thermal stability of complexes is greatly enhanced upon immobilization. The TG data of neat complexes and zeolite-Y based material are presented in Table 5.

Table 4
electronic spectroscopy of neat complexes and zeolite-Y based materials.

Compound	Ind Electronic transition (nm)							
	$\pi  ightarrow \pi^*$	$n \to \pi^*$	MLCT	d-d transition				
$[Co(L^1)]$	282, 272, 266, 233	306	373	869				
$[Cu(L^1)]$	285, 249, 223,	304	352	550				
$[Co(L^2)]$	276, 270, 258, 247	307	384	867				
$[Cu(L^2)]$	287, 258, 241	306	363	551				
Na-Y	-	-	306, 345	-				
Co(II)-Y	-	-	306, 343	-				
Cu(II)-Y	-	-	307, 343	740, 899				
$[Co(L^1)]-Y$	274, 256, 228	288	365, 306, 343,	856				
$[Cu(L^1)]-Y$	277, 245, 222	284	324, 306, 343	521				
$[Co(L^2)]-Y$	281, 254, 228	291	346, 306, 337	851				
$[Cu(L^2)]-Y$	261, 248, 226	293	330, 306, 343	542				



Fig. 5. TGA of the (a) [Co(L<sup>1</sup>)], (b) [Cu(L<sup>1</sup>)], (c) [Co(L<sup>2</sup>)], (d) [Cu(L<sup>2</sup>)], (e) Na-Y, (f) Co(II)-Y, (g) Cu(II)-Y, (h) [Co(L<sup>1</sup>)]-Y, (i) [Cu(L<sup>1</sup>)]-Y, (j) [Co(L<sup>2</sup>)]-Y, (k) [Cu(L<sup>2</sup>)]-Y and (l) dehydrated recycled catalyst [Cu(L<sup>1</sup>)]-Y.

# 4. Catalytic activity

# 4.1.1. Oxidation of cyclohexene

The catalytic oxidation of cyclohexene was performed at optimized reaction condition (25 mmol cyclohexene, 25 mmol 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg Catalyst, 6 mL of acetonitrile, 353 K, 18 h) using each prepared catalysts. As presented in Table 6, the oxidation of cyclohexene is found trivial in the presence of only ligands [28], Na-Y [28], Co(II)-Y and Cu(II)-Y as catalyst, whereas immobilized metal complexes and the neat complexes extensively catalyzed the cyclohexene in the presence of H<sub>2</sub>O<sub>2</sub>. This observation signifies that the metal complexes present in of zeolite-Y nanovoids are playing a vigorous role in catalyzing the substrate. Nevertheless, the immobilized complexes have lesser metal content (%) compared to the respective neat complexes, it efficiently catalyzes the cyclohexene with higher conversion (higher TON) with higher selectivity of allylic products. The conversion (%) of cyclohexene catalyzed by zeolite-Y based catalysts upsurges in the order: Na- $Y < Co(II) - Y < Cu(II) - Y < [Co(L^2)] - Y < [Cu(L^2)] - Y < [Cu(L^1)] - Y [Cu(L^1)] - Y$ Y. According to the trends, the catalyst having lower metal content inside the zeolite-Y nanovoids is found most active compared to the one having higher (%) metal content. This might be due to an easy effective collision of cyclohexene and H<sub>2</sub>O<sub>2</sub> with intensely suppressed metal complexes present in the nanovoids of catalyst having lower metal content compared to the one having higher metal content (%). The above activity trends of the catalysts is also reinforced by the data of H<sub>2</sub>O<sub>2</sub> conversion and H<sub>2</sub>O<sub>2</sub> efficiency carried out separately at identical reaction condition. As presented in the Table 6, the H<sub>2</sub>O<sub>2</sub> conversion is 14.1% at reaction temperature (80 °C), even in the absence of the catalyst due to self-decomposition, whereas the presence of catalysts such as  $H_2L^1$ , H<sub>2</sub>L<sup>2</sup>, and Na-Y has no considerable effect on H<sub>2</sub>O<sub>2</sub> conversion, signifying no role of ligands and zeolite-Y framework in the catalytic activity of immobilized and neat complexes. The use of a catalyst that contains transition metal ion (metal exchanged, immobilized, and neat complexes) drastically increases the conversion of H<sub>2</sub>O<sub>2</sub>, demonstrating the imperative role of transition metals present in the catalyst. The lower H<sub>2</sub>O<sub>2</sub> efficiency and cyclohexene conversion in the presence of Co(II)-Y and/or Cu(II)-Y catalysts could be ascribed to the lower activity of  $H_2O_2$  to react with cyclohexene or quick decomposition of  $H_2O_2$  or the inability of the metal ion to form an active intermediate, which

#### Table 5

Thermogravimetric results of neat complexes and zeolite-Y based materials.

Compound	TG range (°C)	Mass loss % obs. (calc.)	Assignment
[Co(L <sup>1</sup> )]	30-160	01.80	- No considerable mass loss
	161-500	52.30 (53.03)	- Loss of ligands due to complex breakdown
	501-700	45.90 (46.97)	- Cobalt oxide as residue
$[Cu(L^1)]$	30–160	1.50	- No considerable mass loss
	161-450	77.20 (77.89)	- Loss of ligands due to complex breakdown
	451-700	21.30 (22.10)	- CuO as residue
[Co(L <sup>2</sup> )]	30-160	1.55	<ul> <li>No considerable mass loss</li> </ul>
	161–500	59.29 (60.61)	- Loss of ligands due to complex breakdown
	501-700	39.16 (39.39)	- Cobalt oxide as residue
$[Cu(L^2)]$	30–160	1.12	- No considerable mass loss
	161-450	79.71 (81.43)	- Loss of ligands due to complex breakdown
	451-700	19.17(18.56)	- CuO as residue
Na-Y	30-400	10.32	- Loss of physically and chemisorbed water
Co(II)-Y	30-400	09.82	- Loss of physically and chemisorbed water
Cu(II)-Y	30-400	12.12	- Loss of physically and chemisorbed water
$[Co(L^1)]-Y$	30-400	06.63	- Loss of physically and chemisorbed water
	401-700	02.10	- Loss of ligands due to complex breakdown
$[Cu(L^1)]-Y$	30-400	08.22	- Loss of physically and chemisorbed water
	401-700	02.31	- Loss of ligands due to complex breakdown
[Co(L <sup>2</sup> )]-Y	30-400	06.10	- Loss of physically and chemisorbed water
	401-700	02.76	- Loss of ligands due to complex breakdown
$[Cu(L^2)]-Y$	30-400	04.24	- Loss of physically and chemisorbed water
	401-700	02.45	- Loss of ligands due to complex breakdown
$[Cu(L^1)]-Y^a$	30-400	00.56	- Loss of physically and chemisorbed water
	401-700	02.26	- Loss of ligands due to complex breakdown

<sup>a</sup> Before TG analysis, recycled catalyst [Cu(L<sup>1</sup>)]-Y was dehydrated at 300 °C for 2 h.

# Table 6

Oxidation of cyclohexene over various neat complexes and zeolite-Y based catalysts at optimized conditions.

Catalyst	H <sub>2</sub> O <sub>2</sub> Conv. effi. <sup>a</sup> (%) (%)		Cyclohexene	Selectivity	/ (%) <sup>c</sup>		Metal (µmol) in catalyst <sup>h</sup>	TON <sup>i</sup>	
			Conversion <sup>D</sup> (%)	CyOl <sup>d</sup>	CyOne <sup>e</sup>	CyOx <sup>f</sup>	Cydiol <sup>g</sup>		
Nil	14.1	25.4	03.6	28.90	09.18	45.66	16.26	_	-
Co(II)-Y	45.0	25.2	11.3	39.77	41.40	13.55	05.28	1.75	1606
Cu(II)-Y	100	13.2	13.2	32.41	42.18	14.44	10.97	1.98	1641
$[Co(L^1)]$	58.3	86.7	50.6	35.33	46.82	-	17.85	38.0	332.3
$[Cu(L^1)]$	100	76.7	76.1	48.29	48.50	-	03.21	34.9	545.3
$[Co(L^2)]$	45.1	89.8	40.5	36.14	58.52	-	05.34	29.9	338.1
$[Cu(L^2)]$	99.3	62.5	62.1	41.20	56.48	-	02.32	29.4	527.6
$[Co(L^1)]-Y$	100	75.5	75.5	36.73	59.95	-	03.32	1.29	14,612
$[Cu(L^1)]-Y$	100	86.6	86.6	39.02	59.40	-	01.58	0.99	21,708
$[Co(L^2)]-Y$	78.1	72.4	56.5	29.07	66.49	03.83	00.61	1.19	11,808
$[Cu(L^2)]-Y$	94.8	66.9	63.4	35.49	58.62	01.86	04.03	1.25	12,623
$[Cu(L^1)]-Y^j$	100	83.5	85.5	38.78	60.46	-	00.76	1.07	19,566
$[Cu(L^1)]-Y^k$	100	81.1	84.1	39.12	59.12	-	01.76	1.07	18,990
$[Cu(L^1)]Y^l$	100	80.2	83.2	38.90	60.34	-	00.76	1.07	18,792

<sup>a</sup>  $H_2O_2$  efficiency = (moles of product formed/mol of  $H_2O_2$  reacted  $\times$  100.

<sup>b</sup> Conversion means fraction of starting material expended in the reaction.

<sup>c</sup> Selectivity is the production rate of one component per production rate of another component.

<sup>d</sup> 2-Cyclohexen-1-ol.

e 2-Cyclohexen-1-one

<sup>f</sup> Cyclohexene oxide (1,2-epoxycyclohexane).

g Cyclohexene-1,2-diol

<sup>h</sup> Amount of metal atom in µmol present per 12.5 mg of catalyst.

<sup>i</sup> TON (turnover number): Moles of cyclohexene transformed per mole of active metal ion

<sup>j</sup> First reuse of catalyst after dehydrated at 300 °C for 2 h.

<sup>k</sup> Second reuse of catalyst after dehydrated at 300 °C for 2 h.

<sup>1</sup> Third reuse of catalyst after dehydrated at 300 °C for 2 h. Reaction condition: 25 mmol of substrate (cyclohexene), 25 mmol of 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg of Catalyst, 6 mL of CH<sub>3</sub>CN, 353 K, 18 h.

can easily attack the substrates and provides its oxygen to substrates immediately. In the case of neat and immobilized chelate complexes, higher  $H_2O_2$  efficiency, higher cyclohexene and  $H_2O_2$  conversion were observed, which might be facilitated via formation of an active intermediate that can easily attack to the cyclohexene and leads to the higher activity. Moreover, the presence of electron withdrawing groups (chlorine) at the para position to the hydroxyl group in complexes of  $H_2L^2$  ligand decreases an electron deficient metal center compared to the complex of  $H_2L^1$  ligand having no electron withdrawing group (R = H) [42– 44]. Consequently, the complex of  $H_2L^1$  can be simply oxidized to M(III) due to low redox potentials of  $M^{(n + 1)}/M^{(n)}$ . Therefore, the complexes bearing  $H_2L^1$  ligand have been found highly active (higher TON) compared to the complexes of  $H_2L^2$ .

# 4.1.2. Catalyst stability and reusability

The reusability of a heterogeneous catalyst has great importance in designing the appropriate catalyst. The homogeneous  $[Cu(L^1)]$  was readily degraded and could not be recovered even once, whereas zeolite-Y immobilized [Cu(L<sup>1</sup>)]-Y catalyst was easily isolated and reused trice without substantial loss of activity and the selectivity of allylic products (Table 6 last three entries). The catalyst [Cu(L<sup>1</sup>)]-Y was easily isolated from the reaction mixture after first catalytic cycle (oxidation of cyclohexene) by simple filtration, washed with acetonitrile and dehydrated at 300 °C for 2 h before being analyzed by various physicochemical techniques and/or used for successive run. The analogous pattern of XRD (Fig. 1h), FTIR (Fig. 3g) and TGA (Fig. 5l) of recycled  $[Cu(L^1)]$ -Y to the fresh catalyst confirms the conservation of zeolite-Y framework without any kind of destruction during the catalytic oxidation. Moreover, the similar M/C ratio (Table 2) of recycled  $[Cu(L^1)]$ -Y catalyst (0.31) and fresh catalyst (0.31) suggest the absence of metal ion leaching during the catalytic activity and it is further buttressed by the absence (tested by AAS) of metal ion in oxidation products.

# 5. Oxidation of the other organic substrates

Additionally, an afford have been made to sightsee the activity of  $[Cu(L^1)]$  and  $[Cu(L^1)]$ -Y catalysts over benzene, phenol, styrene, benzyl alcohol, limonene,  $\alpha$ -Pinene, cyclohexane and cyclooctane at identical reaction condition. As presented in Table 7, heterogeneous  $[Cu(L^1)]$ -Y catalyst is more active and selective (Table 7, results out of the bracket) as compared to its homogeneous (Table 7, results in the bracket) counterpart  $[Cu(L^1)]$ .

The  $[Cu(L^1)]$ -Y is highly selective (allylic product: 98.4%) and active (86.6% of conversion with TON; 21,708) for oxidation of cyclohexene and therefore, the higher activity and selectivity was anticipated for similar kind of organic substrate having C=C and weak allylic C-H bonds such as limonene and  $\alpha$ -Pinene. However the catalyst can attacks on C==C and weak allylic C–H of limonene or  $\alpha$ -pinene and can produce allylic and epoxide products simultaneously, the presence of the bulky methyl group at C=C may hinder the attack of bulky catalyst at C=C as well as fairly at allylic C-H bond, which reduces the activity of the catalyst for the limonene (11.9%) and  $\alpha$ -pinene (9.2%). Moreover, the high selectivity of allylic products (100%) upon oxidation of limonene and  $\alpha$ -pinene could be accredited to the preference of catalyst to attack at a less hinder site of the substrates (allylic C-H). Because of the absence of bulky group and activated allylic C—H bond in the styrene, mainly epoxide (87.5%) product is obtained due to epoxidation, which immediately hydrolyzed to styrene glycol (66.7%) owed to acidic nature of the host Material [45,46]. The production of benzaldehyde (33.33%) is owing to the later nucleophilic attack of H<sub>2</sub>O<sub>2</sub> on the preformed styrene oxide [47,48].

As presented in Table 7, the catalyst  $[Cu(L^1)]$ -Y is found extremely active for the oxidation of cycloalkanes with the higher selectivity of corresponding cycloalkanone (80–75%) and it is also highly selective towards the formation of hydroquinone (100–87%) from benzene and phenol. Moreover, the catalyst is abstemiously active (21.51%) for oxidation of benzyl alcohol with 55.45% of the benzaldehyde. However, this catalyst is lower active (conversion), it offers higher selectivity

#### Table 7

Oxidation of some other organic substrate over [Cu(L <sup>1</sup>	<sup>1</sup> )](	(homogeneous)	and [	Cu(L	<sup>1</sup> )]-Y	(heterogeneous)	catalysts
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Sr no.	Substrate	Conversion (%)	Selectivity (%)	TON	
1	Cyclohexene	86.6 (76.1)	CyOne: 59.40 (48.50) CyOl: 39.03 (48.29) Cydiol: 01 57 (3.21)	21,708 (545.3)	
2	Cyclohexane	75.2 (61.2)	Cyaone: 80.79 (69.32) Cyaol: 19.21 (30.68)	18,846 (438.1)	
3	Benzene	08.2 (7.3)	Phenol 12.45 (54.32) HQ: 87.55 (45.68)	2054 (68.8)	
4	Phenol	14.5 (11.3)	Cat: 00 (33.00) HQ 100 (67.00)	3636 (81.0)	
5	Styrene	87.5 (70.3)	Bnzald: 33.30 (55.32) Sdiol: 66.70 (44.68)	21,942 (503.1)	
6	Benzyl alcohol	21.5 (19.2)	Bnzald: 55.45 (76.34) Bacid: 44.55 (23.66)	4851 (137.3)	
7	Limonene	11.2 (05.3)	Cone: 93.20 (66.55) Col: 06.80 (33.58)	2829.6 (38.3)	
8	α-Pinene	09.1 (6.8)	Vone: 71.63 (54.22) Vol: 28.37 (45.78)	2293 (48.9)	
9	Cyclooctane	43.2 (35.2)	Coone: 76.89 (67.20) Cool: 23.11 (32.80)	10,836 (252.0)	

*CyOne*: 2-Cyclohexen-1-one, CyOl: 2-Cyclohexen-1-ol, Cydiol: Cyclohexene-1,2-diol, Cyaone: cyclohexanone, Cyaol: cyclohexanol, HQ: hydroquinone, Cat: Catechol, Bnzald: Benzaldehyde, Sdiol: styrene glycol, Bacid: benzoic acid, Cone: carvone, Col: carveol, Vone: verbenone, Vol: Verbenol, Coone: cycloocatanone, Cool: cyclooctanol. TON (turnover number): Moles of substrate transformed per mole of active metal ion, *Reaction condition*: 25 mmol of substrate, 25 mmol of 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg of [Cu(L<sup>1</sup>)]-Y (results out of bracket) and/or [Cu(L<sup>1</sup>)] (results in bracket), 6 mL of CH<sub>3</sub>CN, 353 K, 18 h.

and hence there is wide scope to increase the conversion of these organic substrates by the optimization of the various reaction parameters. Catalytic oxidation of such substrates using various homogeneous and/or heterogeneous catalysts has been studied recently by some other groups (Table 8) and being compared with our catalytic system (Table 7) on the basis of their TON values [49–69]. Except one or two catalytic systems, our catalytic system is found to be more promising and selective for the oxidation of such type of organic substrates.

# 6. Plausible reaction pathway of catalysts

To figure out the plausible reaction pathway and intermediate species encompass during oxidation of the limonene, we have monitored the headway of the reaction using UV–vis spectroscopy by dropwise addition of  $10^{-4}$  M methanolic 30% H<sub>2</sub>O<sub>2</sub> to  $10^{-4}$  M methanolic solution of neat metal complexes. As displayed in Fig. 6a–d, slight upsurges in the intensities of bands present underneath 300 nm, subsiding in the

intensity of the *MLCT* bands, gradual vanishing of *d*-*d* bands, and appearance of new isobestic point (red arrows in Fig. 6a–d) nearly at 344– 313 nm in all neat metal complexes upon consecutive addition  $H_2O_2$ clearly suggests a direct interaction of M(II) center with  $H_2O_2$  and not with limonene in the first step of catalytic pathway, as reported earlier [70,71]. This is further reinforced by the absence of an isobestic point in electronic spectra (Fig. 6e and f) taken during to the progressive addition of  $10^{-4}$  M methanolic solution of limonene to  $10^{-4}$  M methanolic solution of neat [Co(L<sup>1</sup>)] and/or [Cu(L<sup>1</sup>)] complexes.

One of the intermediate having metal-oxygen interaction such as  $bis(\mu-oxo-M^{III})$  or  $M^{III}$ -OOH (metal-hydroperoxide) are likely to be involved during the catalytic oxidation which can transfer its oxygen to the substrate and leads oxyfunctionalized products [72–74]. Out of these two, the involvement of metal hydroperoxide ( $M^{III}$ -OOH) could be left out here due to its lower stability at the present reaction temperature (usually stable at -20 to -50 °C) [75,76] and the absence of  $v_{(O-H)}$  bands in FTIR of solid products (light pink) that is obtained

Table 8

Literature survey of some recently published article for oxidation of organic substrate with their TON values.

Sr. No.	Catalyst	Substrate	Oxidant	Conv.	Major product	TON	Ref.
				(%)	(%)		
1	$[Cu(SFCH) \cdot H_2O] - Y$	Cyclohexane	$H_2O_2$	45.1	Cyaone (84.5)	25.20	49
2	Cu(II) polymer anchored	Cyclohexene	TBHP	83.0	CyOne (64.0)	395.2	50
3	$[MoO_2HL(HOCH_3)])$	Cyclohexene	TBHP	100	CyOX (100)	-	51
4	[VO(L1)(acac)]-Y	Cyclohexene	$H_2O_2$	74.6	CyOne (48.3)	86,790	52
5	[VO(hacen)]-Y	Cyclohexene	$H_2O_2$	91.7	CyOne (50.2)	53,388	28
6	[Mn(sal-2,6-py)]-NaY	Cyclohexene	TBHP	92.5	CyOne (90.8)	-	53
7	Catalyst 5	Cyclohexene	02	53.9	CyOl (72.5)	-	54
8	[Ni((Benzyl) <sub>2</sub> Bzo <sub>2</sub> [14]aneN <sub>6</sub> )] <sup>2+</sup> -NaY	Cyclohexene	02	68.7	CyOl (74.6)	-	55
9	[VO(L1)(acac)]-Y	Benzene	$H_2O_2$	7.40	Phenol (100)	8478	52
10	[TMA]5PMoV	Benzene	$H_2O_2$	27.2	Phenol (100)	-	56
11	[VO(L1)(acac)]-Y	Phenol	$H_2O_2$	23.6	Cat (65.2)	27,324	52
12	$[Ru(STCH) 3H_2O]^+-Y$	Phenol	$H_2O_2$	52.1	Cat (93.2)	244.0	57
13	([Cu-Imace-H][BF])	Phenol	$H_2O_2$	41.3	Cat (62.9)	62.10	58
14	[VO(salen)]-Y	Phenol	$H_2O_2$	32.6	Cat (92.7)	11,640	59
15	[VO((NO <sub>2</sub> ) <sub>2</sub> -haacac)]-NaY	Phenol	$H_2O_2$	44.8	Cat (85.2)	-	60
16	[VO(L1)(acac)]-Y	Styrene	$H_2O_2$	15.4	Bnzald (75.9)	17,832	52
17	[Cu(bipy)Cl <sub>2</sub> ]	Styrene	TBHP	58.6	HAP (37.3)	64.00	61
18	Cu{salnptn(3-OMe) <sub>2</sub> }	Styrene	TBHP	97.0	Bnzald (57)	303.0	62
19	$[Cu(HL_1)(NO_3)]$	Styrene	$H_2O_2$	100	SO (86.0)	1518	63
20	Cu(II) polymer anchored	Styrene	TBHP	97.0	Bnzald (90.0)	461.6	50
21	[MoO <sub>2</sub> HL(HOCH <sub>3</sub> )]	Styrene	TBHP	75.0	SO (65.0)	-	51
22	Cu(II) catalyst	Benzyl alcohol	TBHP	96.0	Bnzald (75.0)	274.2	50
23	YCu(dmgH) <sub>2</sub>	Benzyl alcohol	$H_2O_2$	52.6	Bnzald $(-)$	-	64
24	$[Cu(Me_4[16]aneN_8)]^{2+})NaY$	Benzyl alcohol	$H_2O_2$	73.2	Bnzald (100)	-	65
25	$[VO(L)H_2O]-Y$	Limonene	$H_2O_2$	28.2	Limgly (34.37)	5412	66
26	[VO(VTCH) <sub>2</sub> ]-Y	Limonene	TBHP	97.7	Limgly (45.10)	801.6	67
27	Ti <sub>4</sub> /SiO <sub>2</sub> -D-2	Limonene	TBHP	72.0	Eepo (81.0)	170.4	68
28	Cu(II) polymer anchored	α-Pinene	TBHP	48.0	VOne (55.0)	228.5	50
29	PVW catalyst	Cyclooctane	$H_2O_2$	94.0	СуооН (77.0)	-	69

Conv.: Conversion, Cyaone: cyclohexanone, Cyone: cyclohexenone, CyOx: Cyclohexene oxide (1,2-epoxycyclohexane), Cat: Catechol, Bnzald: Benzaldehyde, HAP: 2-Hydroxy acetophenone, SO: Styrene oxide, Limgly: Limonene glycol, Eepo: endocyclic 1,2-monoepoxide, CyooH: Cyclooctyl hydroperoxide, VOne: Verbenone.



**Fig. 6.** UV-visible spectral studies of (a) neat  $[Co(L^1)]$  (b) neat  $[Co(L^2)]$  (c)  $[Cu(L^1)]$  (d)  $[Cu(L^2)]$  taken during the sequential addition of a methanolic solution of H<sub>2</sub>O<sub>2</sub> and (isobestic point are observed, red arrows in Panels a–d) (e) neat  $[Co(L^1)]$  (f)  $[Cu(L^1)]$  taken during the consecutive addition of a methanolic solution of limonene (no isobestic point in Panels e and f). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

from dropwise addition of  $H_2O_2$  to the methanolic solution of neat  $[Cu(L^1)]$ . Moreover, the appearance of the new  $v_{(Cu-O)}$  band at 462 nm in the FTIR spectrum (Fig. 7b) of product clearly indicates the involvement of  $[(L^1)Cu^{III}-O-O-Cu^{III}(L^1)]$  as an intermediate during the catalytic activity.

Furthermore, the  $[(L^1)Cu^{III}-O-O-Cu^{III}(L^1)]$  is tested as catalyst over limonene oxidation (in the absence of H<sub>2</sub>O<sub>2</sub>) at identical reaction condition (Fig. 7a) to confirm whether the  $[(L^1)Cu^{III}-O-O-Cu^{III}(L^1)]$  is capable to donate its oxygen to the substrate or not. Amazingly, the higher conversion (16.3%) is achieved compared to the reaction catalyzed by neat  $[Cu(L^1)]$  (5.38%) and/or immobilized complex  $[Cu(L^1)]$ -Y (11.29%) in the presence of H<sub>2</sub>O<sub>2</sub> at identical reaction condition. The lower activity of neat and immobilized complexes as compared to  $[(L^1)Cu^{III}-O-O-Cu^{III}(L^1)]$  is supposed to be due to the lower solubility of  $H_2O_2$  with the limonene.

The probable reaction mechanism for the oxidation limonene catalyzed by  $[Cu(L^1)]$  is demonstrated in Scheme 2. In the first step, the catalyst (I) reacts with  $H_2O_2$  to form  $[(L^1)Cu^{III}-O-O-Cu^{III}(L^1)]$  intermediate (II). The  $[(L^1)Cu^{III}-O-O-Cu^{III}(L^1)]$  intermediate (II) is found to be stable and could be isolated easily, its homolytic cleavage could only be facilitated when it directly interact with the less hinder site of limonene and lead an intermediate (III). This homolytic cleavage of the peroxide bond might have occurred due to rise in the back donation from the filled *dII* orbitals of copper to  $\Pi^*$  MOs of the peroxide upon the interaction of the

# (b) Oxidation of limonene using intermediate as catalyst



# (a) FTIR of intermediate [(L<sup>1</sup>)CuOOCu(L<sup>1</sup>)]



Fig. 7. (a) Oxidation of limonene using  $[(L^1)CuOOCu(L^1)]$  as catalyst (b) FTIR of  $[(L^1)CuOOCu(L^1)]$  intermediate



Scheme 2. The merely tentative reaction mechanism for oxidation of limonene with  $H_2O_2$  catalyzed by  $[Cu(L^1)]$ .

electrophilic allylic site of the limonene, which results in intermediate (IV) and highly active nucleophilic free radical (VI) simultaneously. The intermediate (IV) gives carveol (V), whereas intermediate (VI) further attacks on pre-formed carveol (V) and form intermediate (VII) which finally gives carvone (VIII) as main product with the removal of water and revival the catalyst I.

# 7. Conclusion

The immobilization Co (II) and Cu (IV) Schiff base complexes within the nanovoids of zeolite-Y using the flexible ligand method were effectively established and it was supported by various physicochemical (XRD, BET, SEM, TGA, ICP-OES) and spectral studies (FTIR, UV). These prepared and well-characterized material and/or compound were employed as heterogeneous and/or homogeneous catalyst over the oxidation of cyclohexene using 30% H<sub>2</sub>O<sub>2</sub> as a green oxidant to afford allylic products. Moreover, the heterogeneous catalyst  $[Cu(L^1)]$ -Y is found highly selective for oxidation of benzene, phenol, styrene, benzyl alcohol, limonene,  $\alpha$ -Pinene, cyclohexane and cyclooctane with a moderate conversion. These immobilized complexes can be recovered and reused without loss of catalytic activity, making them grander to their homogeneous counterpart.

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