



# Oxidation of cyclohexene catalyzed by Cu(Salen) intercalated $\alpha$ -zirconium phosphate using dry *tert*-butylhydroperoxide

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## ABSTRACT

Cu(Salen) intercalated  $\alpha$ -zirconium phosphate, abbreviated as  $\{\alpha\text{-ZrP}\cdot\text{Cu}(\text{Salen})\}$  was synthesized in situ by the flexible ligand method. The resulting compound was characterized by BET surface area, X-ray diffraction, energy dispersive X-ray analysis, Fourier transform infrared, electron paramagnetic resonance and atomic absorption spectroscopy. The catalytic activity of  $\alpha\text{-ZrP}\cdot\text{Cu}(\text{Salen})$  was tested for the oxidation of cyclohexene using dry *tert*-butylhydroperoxide as an oxidant. In the oxidation reaction, cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone. Influence of various reaction parameters, viz. reaction temperature, catalyst concentration, substrate concentration and oxidant concentration were studied. Under the optimized conditions, oxidation of cyclohexene gave a maximum of 26.71% conversion. The major product followed the order of selectivity: cyclohexanone > cyclohexanol > cyclohexene oxide. Moreover, hot filtration experiments proved that the catalyst was heterogeneous. The catalyst was reused for six cycles.

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## 1. Introduction

The oxidation of hydrocarbons to oxygenic compounds is a pivotal reaction in organic chemistry, both for fundamental research and industrial manufacturing [1,2]. Oxidation of olefins to give oxygen containing value-added products like alcohols, aldehydes, ketones, acids, epoxides, etc. are extremely important and useful reaction in both chemical and pharmaceutical industries [3]. Now, from both economic and environmental points of view, much attention has recently been focused on the aerobic catalytic oxidation of hydrocarbons to oxygenic compounds using metal catalysts. Transition metal complexes are widely used in homogeneous and heterogeneous catalytic oxidations of different alkenes, alkynes, alcohols, halides, phenols, etc. [4,5]. A variety of copper (II) salts are suitable as catalyst or catalyst precursors. In particular, Schiff base complexes of copper (II) have been used as catalysts in the aziridination, cyclopropanation, oxidation of olefins and phenol [6–10]. The Cu(Salen) complex with peroxide as an oxidant has catalyzed the oxidation of cyclohexene but in moderate yield [11].

In the past few decades, there have been significant developments in the application of heterogeneous catalysts for the industrial production of organic chemicals. Heterogeneous

catalysts, which are widely used in industry, have good thermal stability, can be easily separated from the reaction mixture and can be often regenerated and reused. Therefore, heterogenization of homogeneous metal complexes by supporting it on an insoluble support has attracted a lot of interest as a suitable method for solving many practical problems including recovery of the catalyst from reaction mixture and recycling. Transition metal complexes supported on materials such as alumina [12], amorphous silicates [13], polymers [14], zeolites [15], activated carbon [16] and sol-gel [17] are commonly employed in heterogeneous catalysis. However, either leaching or low selectivity was the main problem during their application as catalysts. Karandikar et al. [18] have grafted copper and cobalt Salen compounds on the surface of MCM-41 through aminosilane linker by adduct formation [18]. The stability of the complexes on the surface and the reusability of the catalysts, however, were not examined.

Immobilization of transition-metal complexes on layered compounds by ion-exchange method to synthesize catalysts is better because it provides temperature- and solvent-stable inorganic layered exchangers of known structure as supports [19]. Crystalline  $\alpha$ -zirconium phosphate,  $\text{Zr}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$  ( $\alpha\text{-ZrH}_2\text{P}$ ), a cation exchanger, has a structure of zeolites type cages and it has been extensively studied for its intercalation chemistry, ion exchange properties, catalytic properties and proton conductivity [20–28]. In previous studies we have reported the use of Fe(Salen) intercalation  $\alpha$ -zirconium phosphate as an active, and reusable catalyst for the oxidation of cyclohexene [29]. Herein, we report the

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synthesis of Cu(Salen) intercalated  $\alpha$ -zirconium phosphate via flexible ligand method, abbreviated as  $\alpha$ -ZrP-Cu(Salen). Its catalytic behaviour was studied for oxidation of cyclohexene using dry *tert*-butylhydroperoxide (TBHP) as an oxidant. Neat copper (II) complex has a tendency to stabilize as dimer [30] but intercalation of Cu(Salen) in the layers of  $\alpha$ -zirconium phosphate prevents their dimerisation and allows their stabilization as monomeric active centre.

## 2. Experimental

### 2.1. Materials

Zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), phosphoric acid, hydrofluoric acid, copper acetate, salicylaldehyde, ethylenediamine, benzene and cyclohexene were of reagent grade (E. Merck). Cyclohexene was checked by gas chromatography (GC) to ensure that no oxidation products were present in the substrate. The solution of dry TBHP in benzene (1.12 N) was obtained by careful azeotropic distillation of the aqueous 70% commercial solution of TBHP (E. Merck) and its strength was estimated as described by Sharpless et al. [31]. Benzene (E. Merck), used as solvent, was purified by a known method [32]. The reference sample of products was prepared by the standard procedure [33].

### 2.2. Physical methods and analysis

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer in the  $2\theta$  range of  $5\text{--}15^\circ$  using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at scanning speed  $2^\circ/\text{min}$  with step size  $0.02^\circ$ . Energy dispersive X-ray analysis (EDX) measurements were performed using a JEOL JSM 6100 electron microscope, operating at 20 kV. The Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer model 1750 in KBr. Atomic absorption spectrometer, Shimadzu AA-6800 was used for the estimation of copper. The electronic spectra were recorded on Shimadzu UV-1700 Pharma Spectrophotometer. The surface area (by BET method), pore volume and pore size were determined by adsorption and desorption of nitrogen at the temperature of liquid nitrogen (77 K) using volumetric adsorption set-up (Micromeritics ASAP-2010, USA). The electron paramagnetic resonance (EPR) spectrum was recorded on a Varian E-112, X band spectrometer operated at a microwave frequency of 9.2 GHz at room temperature. The  $g$  value is reported relative to a 2, 2-diphenyl-1-picrylhydrazil (dpph) standard with  $g = 2.0036$ . Analytical gas chromatography was carried out on a Shimadzu Gas Chromatograph GC-14B with dual flame ionization detector (FID) and attached Shimadzu printer having SE-30 ss column at 393 K. The products were identified by GC-MS (Perkin-Elmer Clarus 500 column;  $30 \text{ m} \times 60 \text{ mm}$ ).

### 2.3. Preparation of catalyst

#### 2.3.1. Preparation of $\text{H}_2\text{Salen}$

N, N'-bis(salicylidene)-ethylenediamine ( $\text{H}_2\text{Salen}$ ) was synthesized by dropwise addition of ethylenediamine (10 mmol), to a methanolic solution (40 mL) of salicylaldehyde (20 mmol). The reaction mixture was heated for 1 h in a water bath with a reflux condenser. After cooling, the yellow precipitate of  $\text{H}_2\text{Salen}$  was formed which was filtered out, washed with petroleum ether, dried and characterized. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3014, 2920, 2900 (C-H), 1620–1631 (C=C/N), 1230–1280 (C-O). M.P.: 433 K; yield: 85%. Anal. found: C, 71.58%; H, 6.02%; N, 10.34%; O, 12.06%. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$  (268): C, 71.64%; H, 5.97%; N, 10.45%; O, 11.94%.

#### 2.3.2. Preparation of $\alpha$ -zirconium phosphate

$\alpha$ -Zirconium phosphate (abbreviated  $\alpha$ -ZrH<sub>2</sub>P) was prepared by modified direct precipitation method [34]: 5.5 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved in 80 mL of distilled water, followed by the addition of 4 mL of 40% hydrofluoric acid. Then 46 mL of 85% phosphoric acid was added under continuous stirring with a magnetic stirrer. The mixture was kept for 15 days without disturbing for setting. The precipitate obtained was filtered out and washed with distilled water until the pH of the supernatant liquid became  $\sim 5$ . Then it was dried at 383 K for 24 h. Finally the structure of  $\alpha$ -ZrH<sub>2</sub>P was confirmed by powder XRD.

#### 2.3.3. Preparation of $\alpha$ -ZrP-Cu(II)

The  $\alpha$ -ZrP-Cu(II) was prepared by ion exchange procedure. Hydrogen ions of  $\alpha$ -ZrH<sub>2</sub>P were exchanged by Cu(II) ions from a  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  solution. Stock solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.1 N) was prepared and 100 mL of this solution per gram of  $\alpha$ -ZrH<sub>2</sub>P was refluxed for 24 h at 373 K. Then it was filtered hot through a sintered glass crucible. The clear filtrate was allowed to cool at 298 K and analyzed for their metal ion content by atomic absorption.

#### 2.3.4. Preparation of $\alpha$ -ZrP-Cu(Salen)

Intercalation of Salen into  $\alpha$ -ZrP-Cu(II) to form  $\alpha$ -ZrP-Cu(Salen) was carried out by flexible ligand technique. 70 mmol of Salen was added to 5 g of  $\alpha$ -ZrP-Cu(II) and stirred at 423 K in an oil bath for 4 h under nitrogen gas flow. The resulting material was extracted with methanol using soxhlet extractor to remove excess ligand that remained uncomplexed in the layer  $\alpha$ -ZrH<sub>2</sub>P as well as located on the surface of the  $\alpha$ -ZrH<sub>2</sub>P along with neat complexes, if any. The remaining uncomplexed metal ions in  $\alpha$ -ZrH<sub>2</sub>P 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  $\text{AgNO}_3$  and dried at 383 K. The calcined sample was characterized by XRD, EDAX, BET surface area analysis, FTIR, EPR and Atomic absorption spectroscopy.

## 2.4. Catalytic oxidation of cyclohexene

The catalytic oxidation of cyclohexene was carried out using  $\{\alpha\text{-ZrP-Cu(Salen)}\}$  catalysts in a three-necked round bottom flask (100 mL). In a typical reaction, nitrogen was flushed for 10 min through the flask, which was loaded with benzene (10 mL), cyclohexene (1.64 g, 20 mmol), dry TBHP (3.57 mL, 4 mmol) and dodecane (an internal standard, 0.1 mL). After nitrogen flushing, the catalyst (0.20 g, 0.3 mmol) was added to the contents of the flask, which were heated at 353 K in oil bath for 5 h with continuous stirring. After completion of the reaction, the contents of the flask were cooled in an ice-bath and the catalyst was filtered out and the liquid layer was analyzed quantitatively by a GC using XE-60 ss column at 393 K. The products were identified by GC-MS. The GC-MS analysis revealed that the main products from the reaction are cyclohexene oxide, cyclohexenol and cyclohexenone. Selectivity is always calculated with respect to the converted cyclohexene. The filtered catalyst was further characterized by XRD, EPR and atomic absorption spectroscopy.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

#### 3.1.1. Estimation of metal contents

Synthesis of Cu(Salen) intercalated  $\alpha$ -zirconium phosphate  $\{\alpha\text{-ZrP-Cu(Salen)}\}$  involved the exchange of Cu(II) ions with hydrogen of  $\alpha$ -ZrH<sub>2</sub>P, which was followed by reaction of metal exchanged

**Table 1**  
Chemical composition, physical and analytical data.

Catalyst	Colour	Metal contents (wt%)	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)	<i>d</i> -Spacing (Å)	IR group frequency (cm <sup>-1</sup> )		
							PO <sub>4</sub> <sup>3-</sup>	Zr–O	CH <sub>2</sub> –N
α-ZrH <sub>2</sub> P	White	–	13.58	0.04	116.69	7.40	1044	597	–
α-ZrP·Cu(II)	Blue	20.54	21.19	0.04	83.35	9.50	991	637	–
α-ZrP·Cu(Salen)	Green	20.42	23.62	0.04	67.19	9.87	1012	614	1700–1300

α-ZrH<sub>2</sub>P with H<sub>2</sub>Salen. Here, ligand entered into the layers of α-ZrH<sub>2</sub>P due to its flexible nature and interacted with metal ions. The chemical composition, physical and analytical data of compounds, obtained at different stages of synthesis of catalyst, viz. α-ZrH<sub>2</sub>P, α-ZrP·Cu(II) and α-ZrP·Cu(Salen) (before and after catalytic reaction) are given in Table 1. The colour of α-ZrH<sub>2</sub>P, α-ZrP·Cu(II) and α-ZrP·Cu(Salen) compounds were different due to change in copper content, which was determined by atomic absorption analysis. There was no copper in α-ZrH<sub>2</sub>P and its colour was white. The colour of α-ZrP·Cu(II) became blue due to the presence of copper by 20.54% while the colour of α-ZrP·Cu(Salen) was green due to the presence of Cu(Salen) in which copper was 20.42%.

### 3.1.2. Surface area analysis

The results of surface area analysis of α-ZrH<sub>2</sub>P, α-ZrP·Cu(II) and α-ZrP·Cu(Salen) are incorporated in Table 1. The ion exchange of Cu(II) led to an increase of surface area of α-ZrH<sub>2</sub>P from 13.58 m<sup>2</sup>/g to 21.19 m<sup>2</sup>/g (α-ZrP·Cu(II)). This was due to increase in number of extra-framework cations while replacing hydrogen ions with bivalent Cu(II) cations. The presence of bivalent Cu(II) cations did not increase the pore volume of α-ZrH<sub>2</sub>P. However the pore sizes of α-ZrH<sub>2</sub>P decreased from 116.69 Å to 83.35 Å in α-ZrP·Cu(II). It was also observed that the intercalation of Cu(Salen) on α-ZrP·Cu(II) led to further increase in the surface area of the catalyst, α-ZrP·Cu(Salen), to 23.62 m<sup>2</sup>/g. This was due to the presence of organic ligand. The pore volume of α-ZrP·Cu(Salen) remained the same as 0.04 cm<sup>3</sup>/g while the pore size decreased to 67.19 Å. This was due to coordination of organic ligand with Cu(II) cation.

### 3.1.3. XRD studies

The XRD patterns of α-ZrH<sub>2</sub>P, α-ZrP·Cu(II), α-ZrP·Cu(Salen) (before catalysis) and α-ZrP·Cu(Salen) (after sixth catalytic cycle) are shown in Fig. 1 and their *d*-spacing corresponding to the plane (002) are incorporated in Table 1. The *d*-spacing of the most intense reflection corresponding to the (002) plane of α-ZrH<sub>2</sub>P was 7.40 Å, which was increased to 9.50 Å in α-ZrP·Cu(II). The shifting of 2.1 Å in the *d*-spacing was due to exchange of hydrogen ions by bivalent Cu(II) ions. The value of *d*-spacing further increased to 9.87 Å in α-ZrP·Cu(Salen). The shifting of 0.37 Å in the *d*-spacing of α-ZrP·Cu(Salen) showed intercalation of Cu(Salen), while the presence of unshifted peak suggested that some traces of the α-ZrH<sub>2</sub>P remained without intercalation. Similar results are also reported [35]. The fully loaded phase is isomorphous [36]. The *d*-spacing did not change after six catalytic cycles, but a peak appeared due to phase change of α-ZrH<sub>2</sub>P (Fig. 1). Similar observations are also reported [24,29,35].

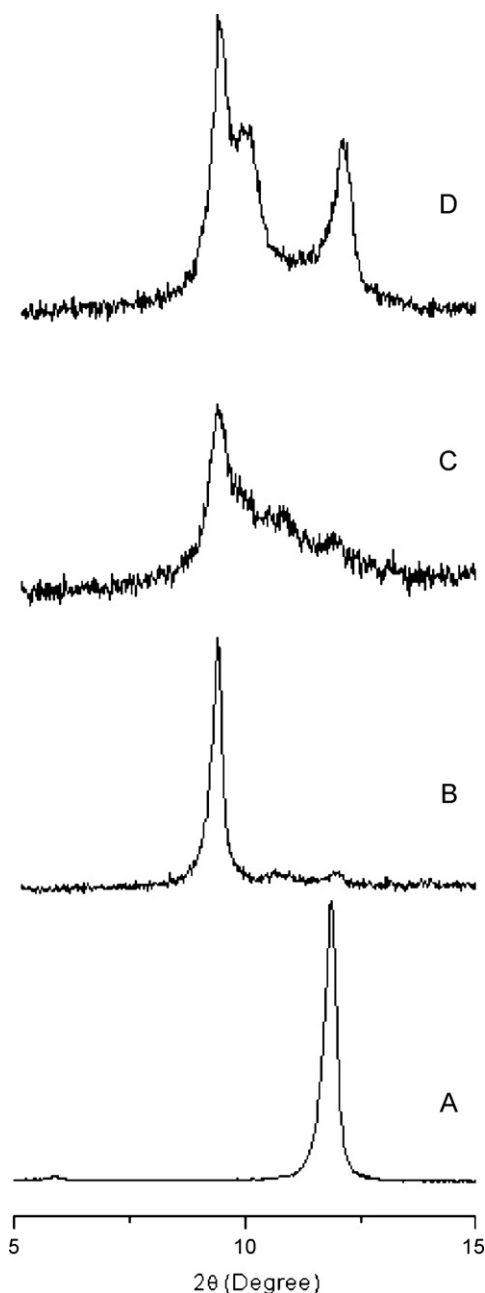
### 3.1.4. EDX analysis

The formation of α-ZrP·Cu(Salen) was confirmed by EDX analysis. The EDX spectra of α-ZrH<sub>2</sub>P, α-ZrP·Cu(II) and α-ZrP·Cu(Salen) are shown in Fig. 2 and EDX measurements results are incorporated in Table 2. The support, α-ZrH<sub>2</sub>P, contained oxygen (81.47%), zirconium (7.09%) and phosphorous (11.44%). The α-ZrP·Cu(II) contained oxygen (79.87%), zirconium (5.48%), phosphorous (8.44%) and copper content (6.21%). The catalyst, α-ZrP·Cu(Salen), contains oxygen (66.19%), zirconium (3.22%), phosphorous (5.67%), copper

(1.68%) and nitrogen (23.24%). The presence of copper and nitrogen indicates the presence of Cu(Salen) on α-ZrH<sub>2</sub>P.

### 3.1.5. FTIR spectral studies

The FTIR spectra of α-ZrH<sub>2</sub>P, α-ZrP·Cu(II) α-ZrP·Cu(Salen) and Cu(Salen), are shown in Fig. 3. The peaks at 3500, 2364 and 1625 cm<sup>-1</sup> in the spectrum of α-ZrH<sub>2</sub>P confirm the presence of



**Fig. 1.** XRD pattern of (A) α-ZrP, (B) α-ZrP·Cu(II), (C) α-ZrP·Cu(Salen)<sup>b</sup>, b: before catalysis and (D) α-ZrP·Cu(Salen)<sup>a</sup>, a: after catalysis.

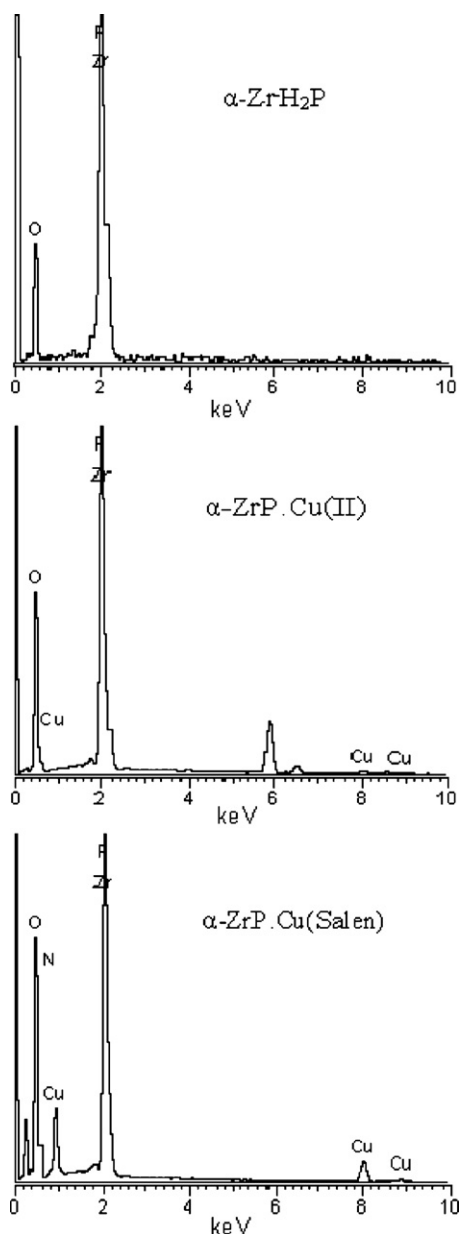


Fig. 2. EDX spectra of  $\alpha\text{-ZrP}$ ,  $\alpha\text{-ZrP.Cu(II)}$  and  $\alpha\text{-ZrP.Cu(Salen)}$ .

external water in addition to the strongly hydrogen-bonded OH or extremely strongly coordinated  $\text{H}_2\text{O}$  [37–39]. The bands appearing at  $1044\text{ cm}^{-1}$  are due to symmetrical stretching vibration of  $\text{PO}_4^{3-}$  and at  $597\text{ cm}^{-1}$  are due to stretching vibration of Zr–O. Detailed band variation data of  $\alpha\text{-ZrH}_2\text{P}$ ,  $\alpha\text{-ZrP.Cu(II)}$ ,  $\alpha\text{-ZrP.Cu(Salen)}$  are listed in Table 1. The band positions of  $\text{PO}_4^{3-}$  in  $\alpha\text{-ZrP.Cu(II)}$  and  $\alpha\text{-ZrP.Cu(Salen)}$  were shifted to lower frequencies while that of Zr–O were shifted to higher frequencies due to the presence of Cu–O interaction and removal of Cu(II) mainly by inner-sphere complex formation with  $\alpha\text{-ZrH}_2\text{P}$  [38]. The peaks in the IR spectrum of Cu(Salen), at  $3195$ ,  $3015$  and  $2923\text{ cm}^{-1}$  are assigned

Table 2  
EDX measurements of  $\alpha\text{-ZrP}$ ,  $\alpha\text{-ZrP.Cu(II)}$  and  $\alpha\text{-ZrP.Cu(Salen)}$ .

Catalyst	O	Zr	P	N	Cu
$\alpha\text{-ZrH}_2\text{P}$	81.47	07.09	11.44	–	–
$\alpha\text{-ZrP.Cu(II)}$	79.87	05.48	08.44	–	06.21
$\alpha\text{-ZrP.Cu(Salen)}$	66.19	03.22	05.67	23.24	01.68

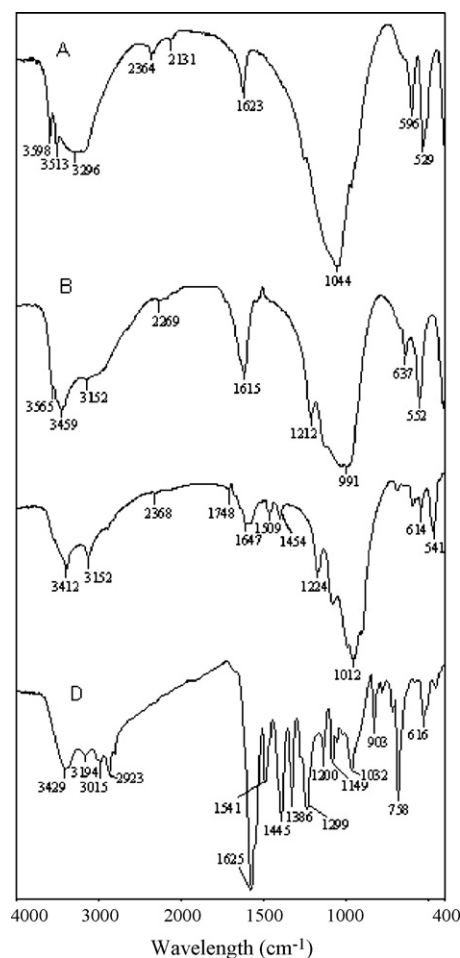


Fig. 3. FTIR spectra of (A)  $\alpha\text{-ZrP}$ , (B)  $\alpha\text{-ZrP.Cu(II)}$  (C)  $\alpha\text{-ZrP.Cu(Salen)}$  and (D) Cu(Salen).

to C–H stretching vibration. The band at  $1630\text{ cm}^{-1}$  due to C=N stretching vibration (of ligand) was shifted to lower frequency and appeared at  $1625\text{ cm}^{-1}$  indicating coordination of the azomethine nitrogen to the Cu(II) ion. The phenolic (C–O) stretching band at  $1230\text{--}1280\text{ cm}^{-1}$  (of ligand) was shifted to higher frequency  $1299\text{ cm}^{-1}$  in Cu(Salen), indicating the coordination through phenolic oxygen. In the IR spectrum of  $\alpha\text{-ZrP.Cu(Salen)}$ , the peaks associated with the  $\text{CH}_2\text{--N}$  bonds of the Salen complex are observed between  $1700$  and  $1300\text{ cm}^{-1}$  region with low intensity, indicating the presence of Cu(Salen).

### 3.1.6. EPR studies

The EPR spectra of randomly oriented powder sample of  $\alpha\text{-ZrP.Cu(II)}$ ,  $\alpha\text{-ZrP.Cu(Salen)}$  before catalytic reaction and  $\alpha\text{-ZrP.Cu(Salen)}$  after sixth catalytic cycle were recorded at room temperature (Fig. 4). Spectral parameters that have been calculated using usual procedure are in good agreement with those reported for copper Schiff base complexes [40]. The average 'g' values obtained for  $\alpha\text{-ZrP.Cu(II)}$ ,  $\alpha\text{-ZrP.Cu(Salen)}$  before catalytic reaction and  $\alpha\text{-ZrP.Cu(Salen)}$  after catalytic reaction were 2.09,

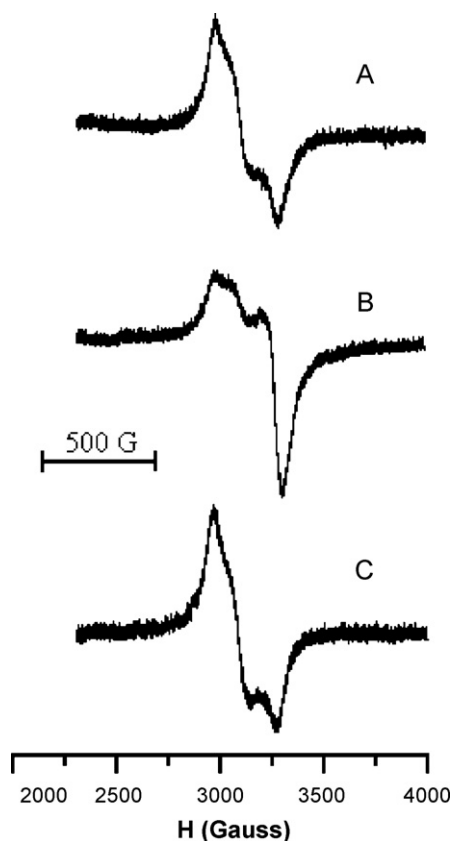


Fig. 4. EPR spectra of (A)  $\alpha$ -ZrP-Cu(II), (B)  $\alpha$ -ZrP-Cu(Salen)<sup>b</sup>, b: before catalysis and (C)  $\alpha$ -ZrP-Cu(Salen)<sup>a</sup>, a: after catalysis.

2.07 and 2.08, respectively (Table 3). The EPR spectrum of powder sample of  $\alpha$ -ZrP-Cu(II) showed axial symmetry with  $g_{\parallel}$  and  $g_{\perp}$  equal to 2.22 and 2.02, respectively, while  $g_{\parallel}$  and  $g_{\perp}$  values for  $\alpha$ -ZrP-Cu(Salen) before catalytic reaction were found to be 2.22 and 2.02, respectively. Hyperfine coupling due to metal ion,  $A_{Cu}$  (for  $^{63}Cu I = 3/2$ ) was not resolved. The ESR spectrum of  $\alpha$ -ZrP-Cu(Salen), taken after catalytic reaction, did not show any change in  $g_{av}$  (2.08),  $g_{\parallel}$  (2.22) and  $g_{\perp}$  (2.01) values. Ratnasamy et al. [41] observed  $g_{\parallel} = 2.269$  and  $g_{\perp} = 2.051$  for Cu(Salen) complexes encapsulated in NaY and suggested square pyramidal geometry for Cu(II), in which Salen ligand provided quadridentate coordination and the zeolite framework (hexagonal prism) provided a strong axial coordination. Therefore, it can be proposed that Cu(II) forms Cu–O bonds with  $\alpha$ -ZrP in  $\alpha$ -ZrP-Cu(Salen) to give either square pyramidal or octahedral geometry around Cu(II) ion due to axial coordination.

### 3.1.7. Electronic spectral studies

The electronic spectra of  $H_2$ Salen (ligand) and Cu(Salen) (complex) are shown in Fig. 5. The electronic spectral data of ligand and complex along with their probable assignments are given in Table 4. The electronic spectrum of the ligand  $H_2$ Salen, recorded in methanol, exhibited three bands at 215, 255 and 316 nm, which are assigned to  $\varphi \rightarrow \varphi$ ,  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The

Table 3  
EPR spectral parameters.

Species	$g_{\parallel}$	$g_{\perp}$	$g_{av}$
$\alpha$ -ZrP-Cu(II)	2.23	2.02	2.09
$\alpha$ -ZrP-Cu(Salen) <sup>b</sup>	2.22	2.00	2.07
$\alpha$ -ZrP-Cu(Salen) <sup>a</sup>	2.22	2.01	2.08

<sup>b</sup> Before catalysis; <sup>a</sup> after catalysis.

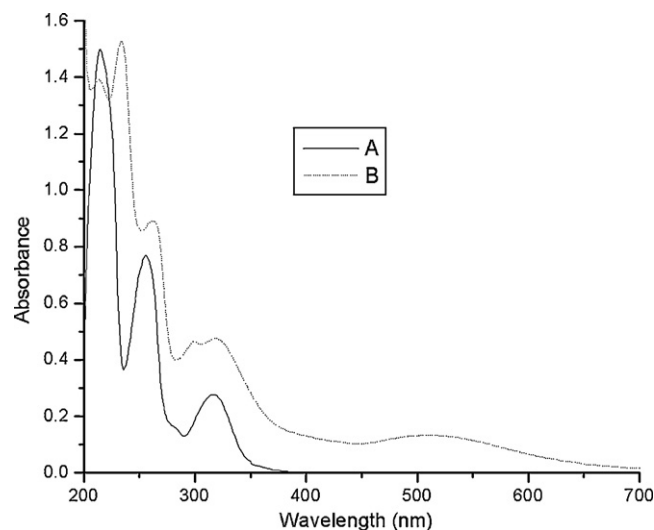


Fig. 5. Electronic spectrum of (A)  $H_2$ Salen and (B) Cu(Salen).

positions of these bands shifted to higher wavelength in Cu(Salen) indicating the coordination of ligand to the metal ions. This is further supported by the appearance of a weak broad band at 510 nm due to d–d transition.

### 3.2. Catalytic oxidation of cyclohexene

The oxidation of cyclohexene with  $\alpha$ -ZrH<sub>2</sub>P, Cu(Salen) and  $\alpha$ -ZrP-Cu(Salen) using dry TBHP as an oxidant were investigated separately under similar experimental conditions. It was observed that  $\alpha$ -ZrH<sub>2</sub>P was catalytically inactive in the oxidation of cyclohexene. The catalyst Cu(Salen) was active for the oxidation of cyclohexene in a homogeneous reaction. In the reaction cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone. The results are incorporated in Table 5. The heterogeneous catalyst,  $\alpha$ -ZrP-Cu(Salen) was developed by intercalation of Cu(Salen) on  $\alpha$ -ZrH<sub>2</sub>P. It was observed that  $\alpha$ -ZrP-Cu(Salen) was active for the oxidation of cyclohexene, which showed that the intercalation of Cu(Salen) converted the non-catalyst,  $\alpha$ -ZrH<sub>2</sub>P, into an active catalyst for the oxidation of cyclohexene. The results of oxidation of cyclohexene  $\alpha$ -ZrP-Cu(Salen) with TBHP as an oxidant are also shown in Table 5. In the cases of both Cu(Salen) and  $\alpha$ -ZrP-Cu(Salen), cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone. The cyclohexenone was the major product in both cases. The conversion of cyclohexene was more in case of Cu(Salen) (30.56%) compared to  $\alpha$ -ZrP-Cu(Salen) (26.71%) however recovery of the catalyst was not possible in the case of Cu(Salen). The yields of the products were based on the internal standard (dodecane) and the consumption of TBHP was determined iodometrically after each catalytic reaction. The

Table 4  
UV-vis data for ligand and complex in methanol.

Compound/solvent	$\lambda_{max}$ (nm)	Assignment
$H_2$ Salen	215	$\varphi \rightarrow \varphi$
	255	$\pi - \pi^*$
	316	$n - \pi^*$
Cu(Salen)	212	$\varphi \rightarrow \varphi$
	264	$\pi - \pi^*$
	318	$n - \pi^*$
	510	d–d transition



**Table 5**  
Effect of support and various catalysts on the oxidation of cyclohexene.

Catalyst	Cyclohexene conversion (%)	Product selectivity (%)		
		Cyclohexene oxide	Cyclohexenol	Cyclohexenone
$\alpha$ -ZrH <sub>2</sub> P	–	–	–	–
Cu(Salen)	30.56	11.38	33.16	55.46
$\alpha$ -ZrP.Cu(Salen)	26.71	03.80	46.40	49.80

amount of dry TBHP consumed and the efficiency of dry TBHP were calculated according to the reported procedure [42] as follows:

$$\text{TBHP consumed (\%)} = \left(1 - \frac{\text{remaining TBHP}}{\text{initial TBHP}}\right) \times 100$$

$$\text{TBHP efficiency (\%)} = \left(1 - \frac{\text{mmol of products}}{\text{mmol of TBHP consumed}}\right) \times 100$$

The selectivity of the products is a measure of the reactivity of the catalyst ( $\alpha$ -ZrP.Cu(Salen)). The percentage-conversion of the substrate and the percentage-selectivity of the products in the oxidation reaction are calculated as

$$\text{substrate conversion (\%)} = \frac{\text{substrate converted (moles)}}{\text{substrate used (moles)}} \times 100$$

$$\text{product selectivity (\%)} = \frac{\text{product formed (moles)}}{\text{substrate converted (moles)}} \times 100$$

The catalytic oxidation of cyclohexene, catalyzed by  $\alpha$ -ZrP.Cu(Salen)/dry TBHP system can be explained by Scheme 1.

Scheme 1 represents the formation of all these products, which are well reported in literature [43–45].

In order to optimize the reaction conditions for the maximum oxidation of cyclohexene the effects of various parameters such as effect of different oxidants, oxidant concentration, substrate concentration, catalyst concentration and temperature were studied in detail.

### 3.2.1. Effect of various oxidants

The effect of various oxidants, viz. H<sub>2</sub>O<sub>2</sub>, TBHP on the oxidation of cyclohexene, catalyzed by  $\alpha$ -ZrP.Cu(Salen) were studied to develop an efficient catalytic system. In each case, the reaction was carried out at 353 K in an oil bath for 5 h with same amount of each oxidant (4 mmol) along with fixed amount of cyclohexene (1.64 g, 20 mmol), catalyst (0.20 g, 0.3 mmol) and dodecane (0.1 mL) in 10 mL of benzene. In case of 30% H<sub>2</sub>O<sub>2</sub> leaching of catalyst was observed. The other oxidants were 70% TBHP and dry TBHP, which effectively oxidized cyclohexene to cyclohexene oxide, cyclohexenol and cyclohexenone. The major product, in both the cases, was cyclohexenone. In case of 70% TBHP, the conversion of cyclohexene was 19.54% and the selectivity of products followed the order: cyclohexenone (64.25%) < cyclohexenol (33.16%) < cyclohexene oxide (2.59%). In case of dry TBHP, the conversion of cyclohexene was 26.71% and the selectivity of products followed the order: cyclohexenone (49.80%) < cyclohexenol (46.40%) < cyclohexene oxide (3.08%). Hence the presence of water has a detrimental effect on the oxidation of cyclohexene [20]. Thus the best oxidant for our catalytic system is dry TBHP, which gave 26.71% cyclohexene conversion.

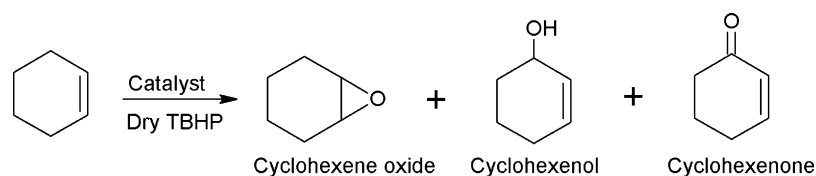
### 3.2.2. Effect of dry TBHP concentration

The concentration of dry TBHP was varied to study its effect on the oxidation of cyclohexene. Three different concentrations (3, 4, and 5 mmol) of dry TBHP were considered while keeping the other parameters fixed as cyclohexene (1.64 g, 20 mmol), catalyst (0.20 g, 0.3 mmol) and dodecane (0.1 mL) in 10 mL of benzene and the reaction was carried out at 353 K in an oil bath for 5 h. The results of the conversion of cyclohexene, consumption of dry

TBHP, efficiency of dry TBHP and selectivity of products are presented in Table 6. Initially conversion of cyclohexene increased sharply from 13.66% for 3 mmol of the dry TBHP to 26.71% for 4 mmol of the dry TBHP, which was the maximum conversion of cyclohexene in our experimental conditions. Further increase in the amount of the dry TBHP to 5 mmol, the conversion of cyclohexene decreased to 24.81%. It was found that when the amount of dry TBHP was changed from 3 to 4 mmol, its efficiency increased from 15.82 to 35.62% while its consumption decreased from 86.34 to 73.29%. When the amount of dry TBHP was further increased to 5 mmol, then its efficiency decreased to 33%, while its consumption decreased to 75.19%. This was probably due to higher oxygen concentration, produced by more oxidant, which inhibited the proceeding of reaction [46]. Cyclohexenone was the major product at all concentration of dry TBHP. The selectivity of cyclohexenone first decreased from 53.64% for 3 mmol of the dry TBHP to 49.80% for 4 mmol, of the dry TBHP then increased to 65.52% for 5 mmol of dry TBHP. The selectivity of cyclohexenol did not show a regular pattern; first increased from 28.76% for 3 mmol to 46.40% for 4 mmol of the dry TBHP, then decreased to 30.74% for 5 mmol of the dry TBHP. The selectivity of cyclohexene oxide first decreased from 17.60% for 3 mmol of the dry TBHP to 3.80% for 4 mmol of the dry TBHP, and then decreased to 3.74% for 5 mmol of dry TBHP. However, the selectivity of cyclohexene oxide was maximum equal to 17.60% at 3 mmol of the dry TBHP. Similar observation is reported in case of  $[-\text{CH}_2\{\text{VO}(\text{sal-dach})\cdot\text{DMF}\}]_n/\text{TBHP}$  system [42]. Thus, a higher concentration of oxidant is not an essential condition to maximize oxidation of cyclohexene. The stoichiometric ratio of the reaction between the dry TBHP and cyclohexene was 5:1. Thus the best concentration of dry TBHP to obtain the maximum conversion of cyclohexene (26.71%) in 5 h reaction time is 4 mmol.

### 3.2.3. Effect of substrate (cyclohexene) concentration

To study the effect of amount of cyclohexene on the oxidation of cyclohexene, the amount of cyclohexene (substrate) was varied from 10 to 25 mmol while keeping the other parameters fixed as oxidant (4 mmol), catalyst (0.20 g, 0.3 mmol) and dodecane (0.1 mL) in 10 mL of benzene and the reaction was carried out at 353 K in an oil bath for 5 h. The results of the conversion of cyclohexene, consumption of dry TBHP, efficiency dry of TBHP and product selectivity for four different concentrations of cyclohexene (10, 15, 20 and 25 mmol) is presented in Table 7. When the concentration of cyclohexene was increased from 10 to 20 mmol, the percentage conversion of cyclohexene also increased from 16.53% to 26.71%. However a further increase in the concentration of cyclohexene to 25 mmol the percentage conversion of cyclohexene decreased to 24.75%. It was found that when the amount of cyclohexene was increased from 10 to 20 mmol, the efficiency of dry TBHP increased from 19.80 to 35.62% while its consumption decreased from 83.47 to 73.29%. Further increase in the amount of cyclohexene to 25 mmol resulted in decreasing the efficiency of dry TBHP to 32.89% whereas its consumption increased to 75.25%. The decrease of the percentage conversion of cyclohexene and the efficiency of dry TBHP at higher concentration of cyclohexene is possibly due to non-availability of oxidant to the substrate. Cyclohexenone was the major product at different concentrations of cyclohexene. The selectivity of cyclohexenone gradually increased from 29.83% for



Scheme 1.

**Table 6**  
Effect oxidant concentration on the oxidation of cyclohexene.

Oxidant conc. (mmol)	Cyclohexene conversion (%)	Dry TBHP consumed (%)	Dry TBHP efficiency (%)	Product selectivity (%)		
				Cyclohexene oxide	Cyclohexenol	Cyclohexenone
3	13.66	86.34	15.82	17.60	28.76	53.64
4	26.71	73.29	35.62	3.80	46.40	49.80
5	24.81	75.19	33.00	3.74	30.74	65.52

**Table 7**  
Effect substrate (cyclohexene) concentration on the oxidation of cyclohexene catalyzed by  $\alpha$ -ZrP-Cu(Salen)/dry TBHP system.

Substrate conc. (mmol)	Cyclohexene conversion (%)	Dry TBHP consumed (%)	Dry TBHP efficiency (%)	Product selectivity (%)		
				Cyclohexene oxide	Cyclohexenol	Cyclohexenone
10	16.53	83.47	19.80	05.40	64.77	29.83
15	17.66	82.34	21.45	03.90	49.32	46.78
20	26.71	73.29	35.62	03.80	46.40	49.80
25	24.75	75.25	32.89	03.78	31.11	65.11

10 mmol of cyclohexene, to 46.78% for 15 mmol of cyclohexene, to 49.80% for 20 mmol of cyclohexene and then to 65.11% for 25 mmol of the cyclohexene. The selectivity of cyclohexenol was maximum 64.77% for 10 mmol of cyclohexene and then gradually decreased to 49.32% for 15 mmol of cyclohexene, to 46.40% for 20 mmol of cyclohexene and then to 31.11% for 25 mmol of the cyclohexene. The selectivity of cyclohexene oxide also showed gradual decrease from 5.40% for 10 mmol of cyclohexene, to 3.90% for 15 mmol of cyclohexene, to 3.80% (20 mmol) and then remains same 3.78% for 25 mmol of cyclohexene. The decrease of the percentage conversion of cyclohexene at higher concentration of cyclohexene is possibly due to non availability of oxidant to the substrate. Thus, a large concentration of substrate with respect of oxidant may reduce the percentage conversion of cyclohexene. The major product at all concentrations of cyclohexene was cyclohexenone. Thus the best concentration of cyclohexene, to obtain the maximum conversion of cyclohexene (26.71%) in 5 h reaction time is 20 mmol.

### 3.2.4. Effect of catalyst concentration

To study the effect of amount of catalyst on the oxidation of cyclohexene, the amount of catalyst,  $\alpha$ -ZrP-Cu(Salen) was varied from 0.10 to 0.40 mmol while keeping the other parameters fixed as cyclohexene (1.64 g, 20 mmol), dry TBHP (4 mmol) and dodecane (0.1 mL) in 10 mL of benzene and the reaction was carried out at 353 K in an oil bath for 5 h. The results of the study for four different concentrations of the catalyst,  $\alpha$ -ZrP-Cu(Salen), viz. 0.10, 0.20, 0.30 and 0.40 mmol are illustrated in Fig. 6. It is evident in Fig. 6 that conversion of cyclohexene increased from 9.78% (0.10 mmol) to 15.64% (0.20 mmol) with the increasing amount of catalyst. When the amount of the catalyst increased to 0.30 mmol, the conversion of cyclohexene increased to 26.71%, which was the maximum conversion of cyclohexene in our experimental conditions. Further increment in the catalyst amount to 0.40 mmol, the conversion of cyclohexene decreased to 24.94%. The conversions of cyclohexene, consumption of dry TBHP, efficiency of dry TBHP and selectivity of various products are presented in Table 8. The increase in the amount of catalyst from 0.10 to 0.30 mmol resulted in increase of the efficiency of dry TBHP from 10.84 to 35.62% whereas its

consumption decreased from 90.22 to 73.29%. Further increase in the amount of catalyst to 0.40 mmol resulted in decreasing the efficiency of dry TBHP to 33.31%, whereas its consumption changed to 75.0%. The reason for reduced activities at higher catalyst dose is possibly due to adsorption/chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact [47]. Cyclohexenone was the major product at different concentrations of catalyst. The selectivity of cyclohexenone first decreased from 73.70% (0.10 mmol) to 71.71% (0.20 mmol) and to 49.80% for 0.30 mmol of the catalyst, then increased to 74.15% for 0.40 mmol of the catalyst. The selectivity of cyclohexenol showed gradual increase from 21.49% (0.10 mmol) to 23.88% (0.20 mmol), to 46.40% (0.30 mmol) of the catalyst, then decreased to 22.07% for 0.40 mmol of the catalyst. The selectivity of cyclohexene oxide showed gradual decrease from 4.81% for 0.10 mmol of the catalyst, to 3.78% for

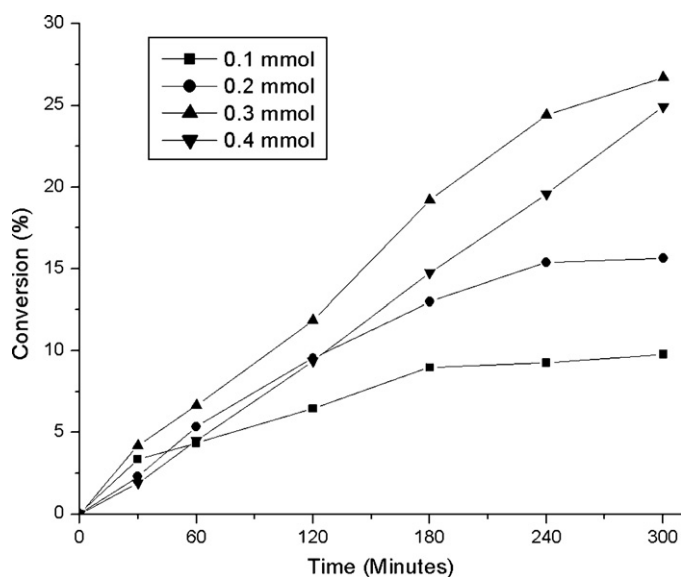


Fig. 6. Effect of catalyst concentration on the conversion of cyclohexene.

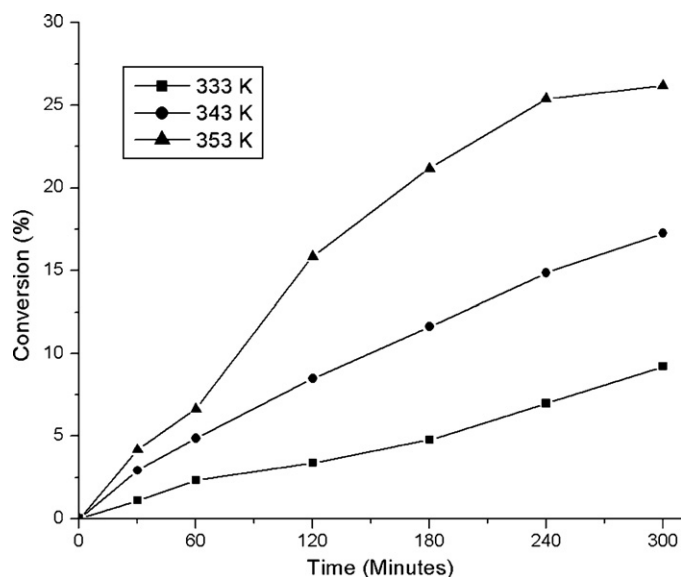


Fig. 7. Effect of temperature on the conversion of cyclohexene.

0.40 mmol of the catalyst. Thus the best concentration of catalyst,  $\alpha$ -ZrP-Cu(Salen), to obtain the maximum conversion of cyclohexene (26.71%) in 5 h reaction time is 0.30 mmol (0.20 g).

### 3.2.5. Effect of temperature

The effect of temperature on the oxidation of cyclohexene was also studied. The reaction was carried out by considering the optimum values of the catalyst (0.20 g, 0.3 mmol), cyclohexene (1.64 g, 20 mmol), dry TBHP (4 mmol) and dodecane (0.1 mL) in 10 mL benzene. The results of three different temperatures, viz. 333, 343 and 353 K are given in Table 9 and Fig. 7. It is evident from Fig. 7 that the catalytic reaction at 353 K had the maximum oxidation of cyclohexene. Also, the reaction reached to its equilibrium in less time at this temperature. It was found that when the temperature increased from 333 K to 353 K, the efficiency of dry TBHP increased from 10.56% to 35.62% whereas its consumption changed from 90.78% to 73.29%. Cyclohexenone was the major product at different reaction temperature. The selectivity of cyclohexenone gradually decreased with increased in temperature from 69.60% at 333 K, to 67.37% at 343 K and then to 49.80% at 353 K. The selectivity of cyclohexenol showed gradual increase from 26.81% (333 K), to 29.02% (343 K) and then to 46.40% (353 K). Similarly, the selectivity of cyclohexene oxide also showed gradual increase from 3.59% at 333 K, to 3.61% at 343 K and then to 3.80% at 353 K. Thus the best reaction temperature, to obtain the maximum conversion of cyclohexene (26.71%) in 5 h reaction time is 353 K.

### 3.2.6. Possible reaction pathway of the catalysts

To establish the possible reaction pathway, the methanolic solution of Cu(Salen) complex was treated with TBHP dissolved in methanol at room temperature and the progress of the reaction was monitored by electronic absorption spectroscopy. Fig. 8 shows the spectral changes upon addition of TBHP in the methanolic

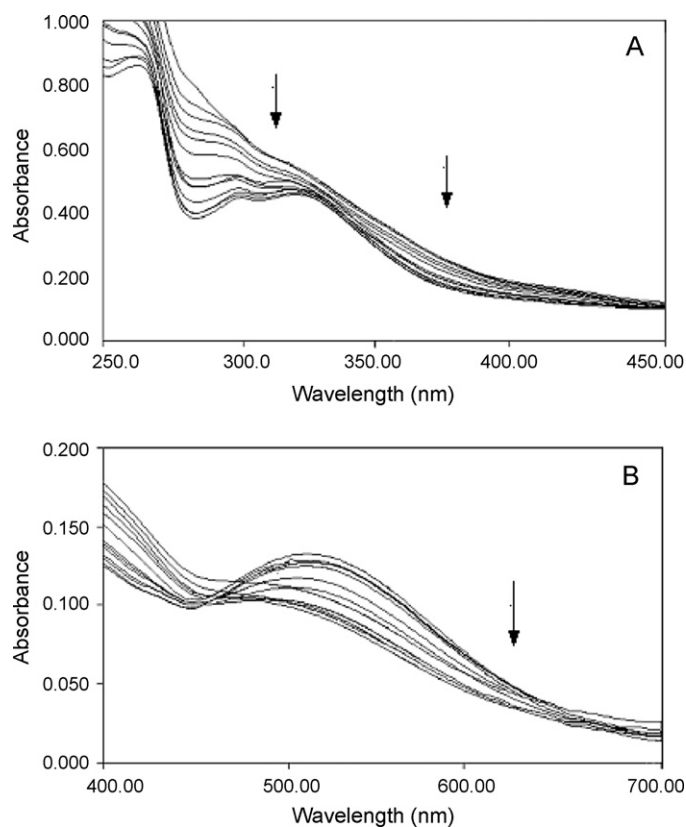


Fig. 8. Titration of [Cu(Salen)] with TBHP(A and B); the spectra were recorded after the successive addition of one drop portions of TBHP to 10 mL of  $10^{-4}$  M solution of [Cu(Salen)] in methanol.

solution of Cu(Salen). It is evident in Fig. 8(A) that the intensity of the 318 nm band increased on dropwise addition of TBHP to  $10^{-4}$  M methanolic solution of Cu(Salen). At the same time the band at 264 nm marginally shifted towards longer wavelength along with broadening and increasing in band maximum. A significant change is observed at the 212 nm (not shown) band, where a large change in the width of the band has taken place along with continuous gain in intensity. A weak broad band appearing at 510 nm (Fig. 8(B)) slowly decreased in intensity without changing its position. The band at 510 nm was due to d-d transition. All these spectral changes suggest the interaction of TBHP with Cu(II) centre. In literature, at least three types of intermediates having copper-oxygen interaction, viz. side-on  $\text{Cu}^{\text{III}}-(\mu-\eta^2\text{-peroxo})-\text{Cu}^{\text{III}}$ , bis( $\mu$ -oxo- $\text{Cu}^{\text{III}}$ ) and  $\text{Cu}^{\text{III}}-\text{O}-\text{O}-\text{H}$  (copper-hydroperoxide) have been reported during catalytic action [48–51]. As Cu(Salen) is monomeric in the  $\alpha$ -ZrH<sub>2</sub>P intercalated copper (II)-Salen complex formation of copper-hydroperoxide species may be expected. The decrease in intensity of 510 nm band with isosbestic point in neat complex may possibly be due to in situ generation of intermediate species, which finally transferred coordinated oxygen atoms to the substrates to give products. Thus, the catalytic performance of intercalated catalyst could be attributed to the formation of facile

Table 8

Effect catalyst concentration on the oxidation of cyclohexene catalyzed by  $\alpha$ -ZrP-Cu(Salen)/dry TBHP system.

Catalyst conc. (mmol)	Cyclohexene conversion (%)	Dry TBHP consumed (%)	Dry TBHP efficiency (%)	Product selectivity (%)		
				Cyclohexene oxide	Cyclohexenol	Cyclohexenone
0.1	09.78	90.22	10.84	04.81	21.49	73.70
0.2	15.64	84.36	18.54	04.41	23.88	71.71
0.3	26.71	73.29	35.62	03.80	46.40	49.80
0.4	24.94	75.01	33.31	03.78	22.07	74.15



**Table 9**  
Effect temperature on the oxidation of cyclohexene catalyzed by  $\alpha$ -ZrP-Cu(Salen)/dry TBHP system.

Temperature (K)	Cyclohexene conversion (%)	Dry TBHP consumed (%)	Dry TBHP efficiency (%)	Product selectivity (%)		
				Cyclohexene oxide	Cyclohexenol	Cyclohexenone
33	09.22	90.78	10.56	03.59	26.81	69.60
343	18.24	98.18	18.58	03.61	29.02	67.37
353	26.71	73.29	35.62	03.80	46.40	49.80

**Table 10**  
Recycling experiment.

No. cycles	Cyclohexene conversion (%)	Product selectivity (%)			Metal contents (%)
		Cyclohexene oxide	Cyclohexenol	Cyclohexenone	
1	26.71	3.80	46.4	49.80	20.42
2	26.70	3.80	46.38	49.82	20.41
3	26.68	3.78	46.36	49.86	20.39
4	26.65	3.78	46.35	49.87	20.36
5	26.59	3.77	46.35	49.88	20.30
6	25.12	3.77	46.30	49.93	19.65

and copper–hydroperoxide species. In fact characteristic charge transfer bands due to Cu–hydroperoxide coordination are known to appear around 590 nm [45,52].

### 3.2.7. Catalytic reusability and heterogeneity of the reactions

It is important to verify the stability of the heterogeneous catalyst since metal leaching from catalyst becomes responsible for lowering of the catalytic activity in successive cycles. To check the reusability of  $\alpha$ -ZrP-Cu(Salen), we have carried out a series of tests by performing repeated reaction cycles under similar reaction conditions as described above. After completion of reaction, the catalyst was recovered by simple filtration, washed with acetone and dried at 383 K and then reused. The catalyst,  $\alpha$ -ZrP-Cu(Salen), was recycled for six cycles. Cyclohexene conversion remained almost identical in the second cycle (26.70%) then dropped to 25.12% after sixth cycle (Table 10 and Fig. 9). The conversion of cyclohexene was reduced by 4.46% from first to sixth cycle. The metal content was reduced by 20.42–19.65% from first to sixth cycle. The reduction in the metal contents after sixth cycle suggests that metal-leaching had occurred, which is observed in several catalytic systems [53–55]. These results suggest that the catalyst was stable during catalytic reaction and suitable for recycling up to sixth cycle. The recycled catalyst was further characterized by XRD and EPR analysis, which also confirmed the stability of the catalyst,

Figs. 1(D) and 4(C). The conversion of cyclohexene decreased due to entrapment of some of the reactant within the layers of the support.

Further experiments on the stability of the catalyst during oxidation of cyclohexene were performed by hot filtration technique. The catalyst was filtered out at 353 K after 1 h in first cycle to avoid re-adsorption of leached copper onto the catalyst surface. Still the reaction took place but with a substantially lower conversion than in the presence of the catalyst. The same solution did not exhibit any colour or the absence of copper, which was estimated using atomic absorption spectroscopy. It suggested that no copper-leaching occurred during the catalytic reaction. This observation indicates that the catalyst is heterogeneous in nature.

## 4. Conclusions

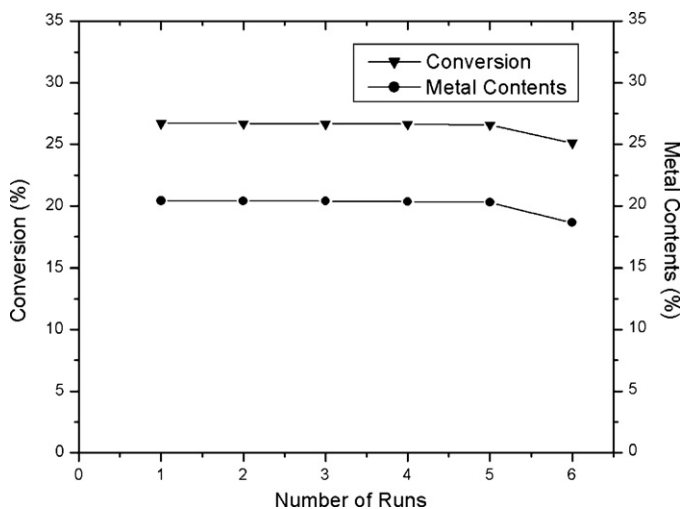
The  $\alpha$ -ZrP-Cu(Salen) was synthesized and characterized by BET surface area, XRD, EDX, FTIR, EPR and atomic absorption spectroscopy. The catalytic activity of  $\alpha$ -ZrP-Cu(Salen) with dry TBHP as an oxidant was studied for the oxidation of cyclohexene. The catalyst,  $\alpha$ -ZrP-Cu(Salen), was found to be a potential catalyst for oxidation of cyclohexene. The reaction conditions were optimized with respect to various parameters to obtain maximum conversion of cyclohexene. The maximum conversion of cyclohexene was 26.71%. The major oxidation products followed the order: cyclohexenone (49.80%) > cyclohexenol (46.40%) > cyclohexene oxide (03.80%). The formation of cyclohexene oxide was low due to its further conversion into other products. The catalyst,  $\alpha$ -ZrP-Cu(Salen), was found to be stable enough for oxidation of cyclohexene for six cycles without much deterioration.

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**Fig. 9.** Recycling of catalyst  $\{\alpha$ -ZrP-Cu(Salen)} for the oxidation of cyclohexene.

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