

# Polymer supported catalysts for oxidation of phenol and cyclohexene using hydrogen peroxide as oxidant

K.C. Gupta\*, A.K. Sutar

*Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee 247667, India*

Received 11 October 2007; accepted 7 November 2007

Available online 17 November 2007

## Abstract

Polymer supported transition metal complexes of *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base were prepared by anchoring its amino derivative Schiff base (AHPHZ) on cross-linked (6 wt%) polymer beads and then loading iron(III), copper(II) and zinc(II) ions in methanol. The loading of HPHZ Schiff base on polymer beads was 3.436 mmol g<sup>-1</sup> and efficiency of complexation of polymer anchored HPHZ Schiff base for iron(III), copper(II) and zinc(II) ions was 83.21, 83.40 and 83.17%, respectively. The efficiency of complexation of unsupported HPHZ Schiff base for these metal ions was lower than polymer supported HPHZ Schiff base. The structural information obtained by spectral, magnetic and elemental analysis has suggested octahedral and square planar geometry for iron(III) and copper(II) ions complexes, respectively, with paramagnetic behavior, but zinc(II) ions complexes were tetrahedral in shape with diamagnetic behavior. The complexation with metal ions has increased thermal stability of polymer anchored HPHZ Schiff base. The catalytic activity of unsupported and polymer supported HPHZ Schiff base complexes of metal ions was evaluated by studying the oxidation of phenol (Ph) and epoxidation of cyclohexene (CH). The polymer supported metal complexes showed better catalytic activity than unsupported metal complexes. The catalytic activity of metal complexes was optimum at a molar ratio of 1:1:1 of substrate to oxidant and catalyst. The selectivity for catechol (CTL) and epoxy cyclohexane (ECH) in oxidation of phenol and epoxidation of cyclohexene was better with polymer supported metal complexes in comparison to unsupported metal complexes. The energy of activation for oxidation of phenol (22.8 kJ mol<sup>-1</sup>) and epoxidation of cyclohexene (8.9 kJ mol<sup>-1</sup>) was lowest with polymer supported complexes of iron(III) ions than polymer supported Schiff base complexes of copper(II) and zinc(II) ions.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Catalysis; Metal complexes; Phenol; Cyclohexene; Epoxidation

## 1. Introduction

The transition metal complexes are frequently used as homogeneous catalysts in various reactions such as epoxidation of olefins [1,2], oxidation of phenols [3,4] and coupling reactions [5], but in these processes, the separation of catalysts from the reaction mixture is difficult in comparison to supported catalysts, which are separated easily without any significant loss in their catalytic activity [6,7]. The supported metal complexes also showed high catalytic activity [8,9] and selectivity [10] in comparison to unsupported complexes. Although various supports [11–15] have been tried to anchor metal complexes, but polymer supports provided better control on activity and selectivity of metal complexes [1,16,17]. The metal complexes on

various supports have been anchored either physically [18,19] or by forming a bond between metal complexes and the supports [20–22], but the recycling of physically anchored catalysts produced inactive catalyst in comparison to bonded catalyst. Unsupported metal complexes of  $\beta$ -diketones [23] and salen [18] Schiff bases showed low activity and enantioselectivity in epoxidation of olefins in comparison to supported metal complexes [6,10,24–26]. Polymer supported Schiff base complexes of metal ions showed high catalytic activity in decomposition of hydrogen peroxide [27] and in oxidation of phenol in presence of *t*-butyl hydroperoxide [28]. Although unsupported metal complexes were used in oxidation of phenol and epoxidation of olefins in presence of hydrogen peroxide [29,30], but supported metal complexes showed high activity in these reactions [31] and in epoxidation of cyclohexene with *t*-butyl hydroperoxide [32,33]. Although zinc(II) ions complexes have been used as catalyst in various reactions, viz., hydrolysis of *p*-nitrophenyl acetate and *p*-nitrophenyl picolinate [34],

\* Corresponding author. Tel.: +91 1332285325.

E-mail address: [kcgptfey@iitr.ernet.in](mailto:kcgptfey@iitr.ernet.in) (K.C. Gupta).

epoxidation of olefins [35], ring opening polymerization (ROMP) of caprolactum [36] and hetero-Diels reactions [37], but have used less commonly than Schiff base complexes of other metal ions [38–41]. Although Schiff base ligands of hydrazine with *o*-hydroxy acetophenone were used for complexation with transition metal ions to produce metal complexes with twisted ligands around N–N bond, but no catalytic activity of these metal complexes was studied [42]. In these investigations, *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base was synthesized by using hydrazine and *o*-hydroxy acetophenone in 1:2 mole ratio, which subsequently produced unsupported and polymer supported metal complexes in 1:1 mole ratio of HPHZ Schiff base ligand and metal ions as proposed on the basis of their characterization. Since no report is available for catalytic activity of unsupported and polymer supported metal complexes of *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base; hence, efforts were also made to evaluate the catalytic activity of unsupported and polymer supported HPHZ Schiff base complexes of iron(III), copper(II) and zinc(II) ions in oxidation of phenol and epoxidation of cyclohexene using hydrogen peroxide as oxidant. The catalytic activity of these complexes was evaluated under different experimental conditions and reaction mechanism for oxidation of phenol and epoxidation of cyclohexene was proposed.

## 2. Experimental

### 2.1. Materials

Chloromethylated polystyrene beads with fixed cross-linked density (6.0 wt%) were obtained from ion exchange India Ltd., Mumbai, India. Anhydrous chloro salts of iron(III), copper(II) and zinc(II) ions were received from Ranbaxy, Mumbai, India, and used without further purification. Cyclohexene, phenol, hydrogen peroxide (30 wt%), *o*-hydroxy acetophenone and hydrazine were procured from E. Merck, India. All other chemicals and solvents were of analytical grade (>99%) and used after purification using standard methods [43].

### 2.2. Characterization of Schiff base and its metal complexes

IR spectra of synthesized HPHZ Schiff base and its metal complexes were recorded on KBr pellet using PerkinElmer 1600 FTIR Spectrophotometer and electronic spectra were recorded with Shimadzu 1601 PC UV–vis Spectrophotometer. Thermogravimetric analysis (TGA) of HPHZ Schiff base and its metal complexes was carried out using PerkinElmer Thermal analyzer (Pyris Diamond) at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. The metal ions complexation with HPHZ Schiff base was determined using Atomic Absorption Spectrophotometer (PerkinElmer Model 3100) at corresponding wave length ( $\lambda_{\text{max}}$ ) of metal ions. The magnetic moment ( $\mu$ ) of metal complexes was measured using vibrating sample magnetometer (Model-155). The molecular weights of HPHZ Schiff base and its metal complexes were measured with Vapor Pressure Osmometer (Knauer K-700, Germany) using

dimethyl formamide (DMF) as solvent and benzyl as a standard.

### 2.3. Synthesis of *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine Schiff base and its metal complexes

*N,N'*-bis (*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base was prepared by modifying the reported procedure [42]. The reaction mixture containing *o*-hydroxy acetophenone (20 mmol, 2.72 g) and hydrazine (10 mmol, 0.16 g) in methanol was refluxed at 60 °C for about 45 min. The reaction mixture after cooling at low temperature produced light yellow colored crystals, which were filtered and recrystallized with methanol. Metal complexes of synthesized HPHZ Schiff base were prepared refluxing 100 mL methanolic mixture of Schiff base (10 mmol, 2.683 g) and metal ions (10 mmol) at 70 °C. After 8 h, the mixture was cooled and crystallized metal complexes were separated from mother liquor. Finally these metal complexes were recrystallized in methanol and dried at 50 °C in vacuum oven.

### 2.4. Synthesis of polymer anchored *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine Schiff base and its metal complexes

To prepare polymer anchored metal complexes of *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base, the amino derivative of HPHZ Schiff base was synthesized by following nitrosation and reduction reactions. Nitrosation was carried out using 10 mmol (2.683 g) of HPHZ Schiff base and 10 mmol sodium nitrite in 10 mL 1.0N hydrochloric acid at low temperature. The resultant *N,N'*-bis (4-nitroso-*o*-hydroxy acetophenone) hydrazine Schiff base was filtered and washed with hot and cold water to remove reaction impurities. Subsequently, the reduction of *N,N'*-bis (4-nitroso-*o*-hydroxy acetophenone) hydrazine was carried out using 10.0 mmol (3.263 g) of nitrosated HPHZ Schiff base in 20.0 mL (1.0N) hydrochloric acid in presence of metallic iron, which produced *N,N'*-bis (4-amino-*o*-hydroxy acetophenone) hydrazine (AHPHZ) Schiff base. Amino functionalized Schiff base (AHPHZ) was immobilized on polymer beads by refluxing 10.0 mmol (5.967 g) of *N,N'*-bis (4-amino-*o*-hydroxy acetophenone) hydrazine with methanol swollen beads (5.0 g) in 50 mL methanol. After 8 h, the HPHZ Schiff base anchored polymer beads were separated and dried in vacuum oven. The HPHZ Schiff base anchored polymer beads were subsequently used for loading of metal ions by keeping 5.0 g HPHZ Schiff base anchored polymer beads in 50 mL methanol containing 10.0 mmol metal ions and then refluxing for 6.0 h at 60 °C. Finally the metal ions loaded polymer beads were separated and washed with hot and cold water and dried in vacuum oven at 70 °C. The loading of metal ions on unsupported and polymer supported HPHZ Schiff base was calculated as efficiency of complexation (%EC) using following equation:

$$\%EC = \frac{\text{Amount of metal ions loaded}}{\text{Amount of Schiff base used for loading}} \times 100$$

### 2.5. Catalytic activity of metal complexes in oxidation of phenol and epoxidation of cyclohexene

To evaluate the catalytic activity of unsupported and polymer supported metal complexes of HPHZ Schiff base, the oxidation of phenol and epoxidation of cyclohexene was carried out using hydrogen peroxide as oxidant. To carry out these reactions, a calculated amount of metal anchored polymer beads was taken in two-necked round-bottomed flask containing phenol (50 mmol, 4.70 g), 2.0 mL acetonitrile, cyclohexene (50 mmol, 4.10 g) dissolving in 2.0 mL chlorobenzene and then calculated volume of hydrogen peroxide (30 wt%) was added in the reaction mixture (88 mmol, 5.67 g). The reaction flask was fitted with water condenser, nitrogen inlet and heated at constant temperature (70 °C) and to increase the activity of polymer beads, the reaction mixture was vigorously stirred (1200 rpm). To follow these reactions, the reaction mixtures were analyzed at different time intervals using gas chromatograph. To analyze cyclohexene (CH) and epoxy cyclohexane (ECH) in the reaction mixture, the gas chromatograph was fitted with 1 m column packed with W-DMCS chromosorb with liquid SE-30 phase of about 2.5 and 0.03% PEG-2000. The temperature of injection port and column was maintained at 150 and 85 °C, respectively, and carrier gas was supplied at 20 mL min<sup>-1</sup>. For analysis of phenol (Ph), catechol (CTL) and hydroquinone (HQ), a fused silica capillary column (XE-60, 30 m × 0.2 mm × 0.3 μm) was used. The temperature of injection port and column was 280 and 180 °C, respectively, and carrier gas was supplied at 20 mL min<sup>-1</sup>. Oxidation of phenol and epoxidation of cyclohexene was also studied at different molar ratios of reactants and at different temperatures to determine the energy of activation for oxidation and epoxidation. These reactions were also studied without using catalysts to determine the effect of catalyst in oxidation of phenol and epoxidation of cyclohexene. The retention time of standards was used to identify the reaction products and peak areas in the chromatograms were used to estimate the amount of reaction products. The amount of reaction products was compared with percent conversion of phenol and cyclohexene.

### 3. Results and discussion

Anchoring of metal complexes on polymer supports has increased the catalytic activity of metal complexes and their reuse applications. Catalytic activity of supported metal complexes also showed variation with nature of polymer support and the amount of metal complex loaded on polymer supports [44,45].

The activity of supported metal complexes was also influenced by their thermal stability and interactions with reactants. The increase in thermal stability of polymer anchored HPHZ Schiff base after complexation with metal ions has been used as evidence for loading of metal ions. The temperature of maximum rate of decomposition ( $T_{max}$ ) of polymer anchored Schiff base (P-HPHZ) and its iron(III) ions complexes was increased from 221 to 336 °C, whereas the increase in  $T_{max}$  was 309 and 340 °C, respectively, on complexation of P-HPHZ Schiff with copper(II) and zinc(II) ions, respectively (Fig. 1). This variation

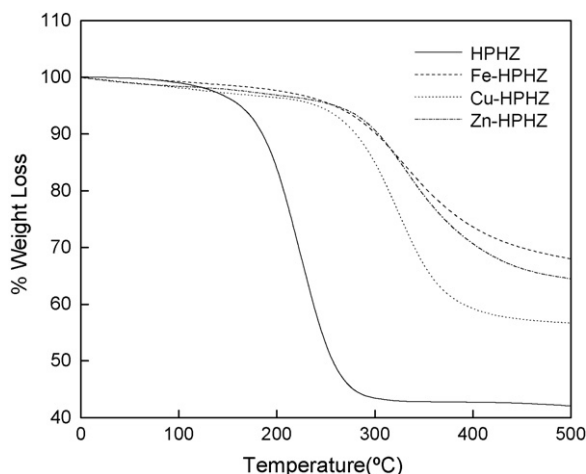


Fig. 1. Thermal stability of polymer supported HPHZ Schiff base and its metal complexes.

in  $T_{max}$  has clearly indicated that zinc(II) ions complexes were more stable than iron(III) and copper(II) ions complexes of polymer anchored HPHZ Schiff base. The polymer anchored HPHZ Schiff base has shown a weight loss of 45% at 300 °C, whereas its metal complexes have shown a maximum weight loss of 5% at same temperature (Fig. 1), which clearly indicated that the complexation of metal ions has increased thermal stability of HPHZ Schiff base.

#### 3.1. Characterization of *N,N'*-bis(*o*-hydroxy acetophenone) hydrazine Schiff base

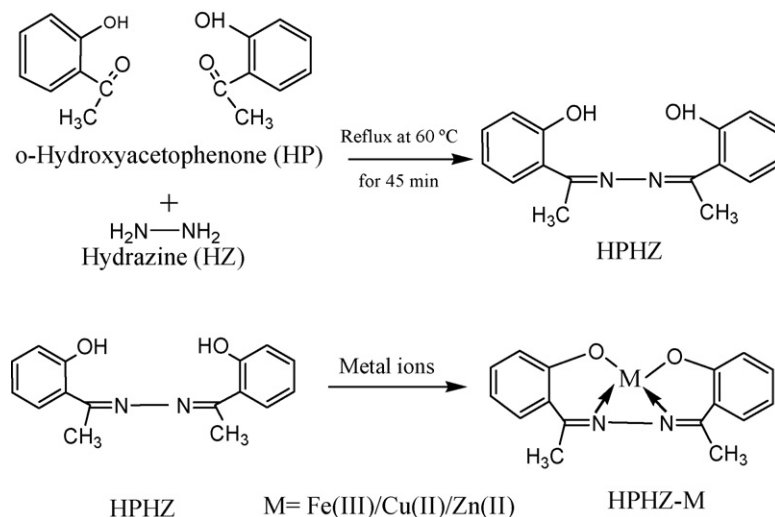
*N,N'*-bis(*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base was obtained by refluxing hydrazine and *o*-hydroxy acetophenone at 60 °C in methanol, which produced a substantial yield (81.79%) of HPHZ Schiff base (Scheme 1).

The IR spectrum of HPHZ Schiff base has shown absorption bands at 1621 and 1268 cm<sup>-1</sup> for >C=N and >C=O (phenolic) groups (Fig. 2A) and a broad band between 3300 and 2950 cm<sup>-1</sup> was due to phenolic OH. The elemental analysis of HPHZ Schiff base (Table 1) was corresponded to C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> empirical formula of HPHZ Schiff base. The molecular weight of Schiff base was found to be 268.22 g mol<sup>-1</sup> (calcd. 268.31 g mol<sup>-1</sup>).

The electronic spectra of HPHZ Schiff base (Fig. 3) showed absorption bands at 248 and 317 nm due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The <sup>1</sup>H NMR spectrum of HPHZ Schiff base showed proton signals at  $\delta$ , ppm = 2.15(3H), 5.15(1H), 6.95(2H), 7.25(1H) and 7.55(1H), which corresponded to structure of HPHZ Schiff base as shown in Scheme 1.

#### 3.2. Synthesis and characterization of *N,N'*-bis(4-amino-*o*-hydroxy acetophenone) hydrazine Schiff base and its anchoring on polymer beads

Nitrosation of *N,N'*-bis(*o*-hydroxy acetophenone) hydrazine Schiff base was carried out at low temperature in presence of NaNO<sub>2</sub>/HCl, which resulted in 86.79% yield of *N,N'*-bis(4-nitroso-*o*-hydroxy acetophenone) hydrazine (Scheme 2). The



Scheme 1. Synthesis of *N,N'*-bis (*o*-hydroxy acetophenone) hydrazine Schiff base (HPHZ) and its metal complexes (HPHZ-M).

Table 1  
Elemental analysis of HPHZ Schiff base its derivatives and metal complex (HPHZ-M)

Schiff base	Elemental analysis (%)				$M_w$ (g mol <sup>-1</sup> )	$\mu$ (BM)
	H	C	N	M		
HPHZ	6.05 (6.03)	71.81 (71.84)	10.42 (10.47)	–	268.2 (268.3)	–
NO-HPHZ	4.33 (4.35)	59.21 (59.18)	17.26 (17.25)	–	324.9 (324.7)	–
A-HPHZ	6.06 (6.09)	64.52 (64.59)	18.80 (18.83)	–	297.1 (297.5)	–
Fe-HPHZ	3.61 (3.59)	48.90 (48.99)	7.11 (7.14)	14.22 (14.24)	392.0 (392.3)	1.73
Cu-HPHZ	4.22 (4.29)	58.37 (58.40)	8.49 (8.51)	19.22 (19.31)	329.0 (329.1)	1.73
Zn-HPHZ	4.24 (4.26)	58.04 (58.08)	8.43 (8.47)	19.70 (19.76)	330.6 (330.9)	0.00

The values in parenthesis are theoretical.

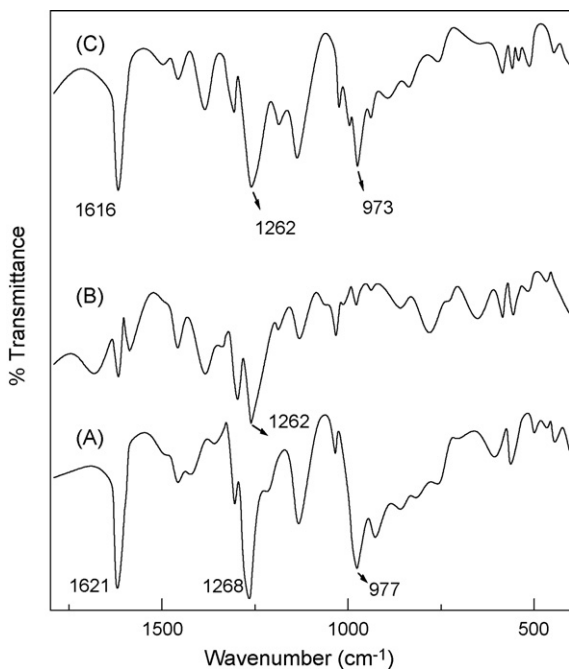


Fig. 2. FTIR spectra of free HPHZ Schiff base (A), polymer beads (B) and polymer anchored Schiff base (C).

elemental analysis of *N,N'*-bis (4-nitroso-*o*-hydroxy acetophenone) hydrazine Schiff base (Table 1) was corresponding to C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub> empirical formula of nitrosated Schiff base. The molecular weight of *N,N'*-bis (4-nitroso-*o*-hydroxy acetophenone) hydrazine was found to be 298.5 g mol<sup>-1</sup> (calcd. 298.3 g mol<sup>-1</sup>). The IR spectrum of *N,N'*-bis (4-nitroso-*o*-hydroxy acetophenone) hydrazine showed absorption bands at 1630 and 1280 cm<sup>-1</sup> for >C=N and >C-O (phenolic) functional

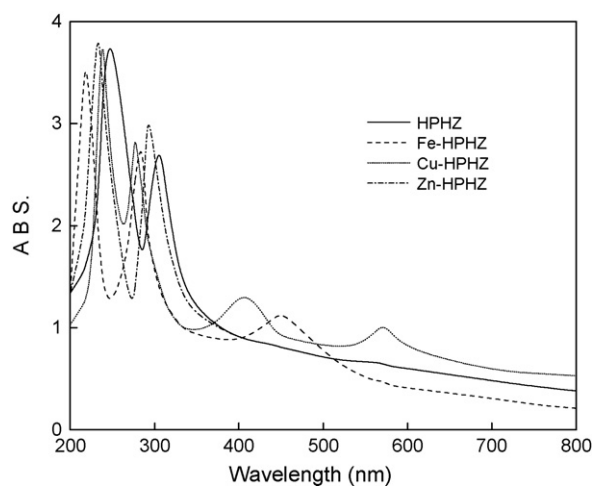
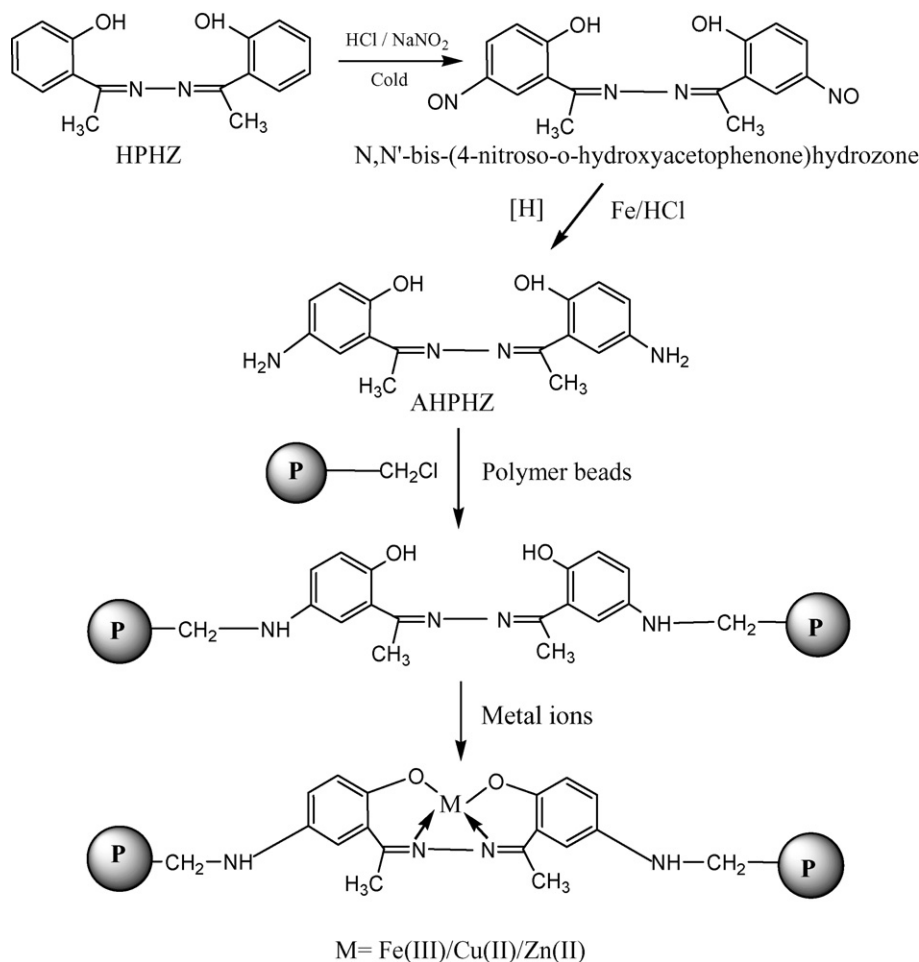


Fig. 3. Electronic spectra of HPHZ Schiff base and its metal complexes.



Scheme 2. Synthesis of polymer anchored Schiff base (P-HPHZ) and its metal complexes (P-HPHZ-M).

groups and absorption bands at 1550 and 1335  $\text{cm}^{-1}$  were due to N–O group. The nitrosation of HPHZ Schiff base has shown a shift in NMR signals in comparison to NMR signals of HPHZ Schiff base. The nitrosated HPHZ Schiff base has given proton signals at  $\delta$ , ppm = 1.05(3H), 5.15(1H), 7.20(1H), 7.82(1H) and 8.15(1H), which were corresponding to the structure of nitrosated Schiff base as shown in Scheme 2. The proton signals *ortho* to nitroso group in nitrosated HPHZ Schiff base were deshielded; hence, appeared at 7.82 ppm and at 8.15 ppm in place of 7.27 and 7.60 ppm of pure HPHZ Schiff base. The absence of proton signal at 7.0 ppm was due to the substitution of nitroso group in the benzene. The reduction of *N,N'*-bis (4-nitroso-*o*-hydroxy acetophenone) hydrazine with iron metal in presence of hydrochloric acid, has produced 85.82% of *N,N'*-bis (4-amino-*o*-hydroxy acetophenone) hydrazine Schiff base (AHPHZ). The resultant AHPHZ Schiff base was characterized for its mp, which was 189 °C. Elemental analysis of *N,N'*-bis (4-amino-*o*-hydroxy acetophenone) hydrazine Schiff base was corresponding to C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> empirical formula of AHPHZ Schiff base. The molecular weight of AHPHZ Schiff base was 299.1 g mol<sup>-1</sup> (caltd. 298.3 g mol<sup>-1</sup>). The IR spectrum of *N,N'*-bis (4-amino-*o*-hydroxy acetophenone) hydrazine Schiff base showed absorption bands at 1621 and 1268  $\text{cm}^{-1}$  due to >C=N and >C-O (phenolic) groups and a band between 1633 and

1650  $\text{cm}^{-1}$  was assigned to >C-N group. The NMR spectrum of AHPHZ Schiff base showed proton signals at  $\delta$ , ppm = 2.15(3H), 4.15(2H), 5.15(1H), 6.45(1H), 6.65(1H), 6.85(1H), which were corresponding to AHPHZ Schiff base structure as shown in Scheme 2.

Refluxing of *N,N'*-bis (4-amino-*o*-hydroxy acetophenone) hydrazine (AHPHZ) Schiff base with cross-linked polymer beads resulted in 85.82% loading of AHPHZ Schiff base, which was corresponding to 3.436 mmol of HPHZ Schiff base on 1 g of polymer beads (Scheme 2). The loading of HPHZ Schiff base on polymer beads was confirmed by comparing IR spectrum of HPHZ anchored polymer beads (Fig. 2C) with IR spectrum of pure polymer beads (Fig. 2B). The IR spectrum of polymer anchored HPHZ Schiff base (Fig. 2C) has shown new absorption bands at 1616 and 1260  $\text{cm}^{-1}$  for >C=N and >C-O (phenolic) groups and a broad band between 2955 and 3373  $\text{cm}^{-1}$  for >C-N group, which were absent in IR spectrum of pure polymer beads (Fig. 2B), but were present in unsupported HPHZ Schiff base (Fig. 2A). The IR spectrum of pure polymer beads has shown absorption band at 1262  $\text{cm}^{-1}$  (Fig. 2B), due to the presence of C–Cl group in polymer beads, which reduced significantly in HPHZ Schiff base loaded polymer beads (Fig. 2C). This variation in absorption band was an evidence for anchoring of HPHZ Schiff base on polymer beads. In addition to these spectral

Table 2

Efficiency of complexation of metal ions (%EC) on unsupported (HPHZ) and supported Schiff base (P-HPHZ)

Schiff base	Iron(III) ions (%)	Copper(II) ions (%)	Zinc(II) ions (%)
HPHZ	80.28	82.28	81.51
P-HPHZ	83.21	82.40	83.17

variations, the appearance of new bands and a shift in absorption bands of HPHZ Schiff base on polymer beads have confirmed the anchoring of HPHZ Schiff base on polymer beads.

### 3.3. Characterization of free and polymer anchored metal complexes of *N,N'*-bis(*o*-hydroxy acetophenone) hydrazine Schiff base

Complexation of metal ions on unsupported (Schemes 1) and polymer supported HPHZ Schiff base (Schemes 2) was carried out by refluxing unsupported and polymer supported HPHZ Schiff base in solution of metal ions at 60 °C for 6 h. The metal anchored Schiff base (HPHZ-M) and polymer beads (P-HPHZ-M) were purified after separation and characterized for molecular weights, magnetic moment and composition by elemental analysis (Table 1). The reaction yield and elemental and molecular weight analysis of metal complexes of HPHZ Schiff base has suggested for 1:1 stoichiometric ratio of HPHZ Schiff base to metal ions like lanthanides [46], and both nitrogen atoms of HPHZ Schiff base were coordinating directly with metal ions without any twisting about N–N single bond of HPHZ Schiff base as found with dinuclear complexes of transition metal ions [42]. The efficiency of complexation of unsupported and supported HPHZ Schiff base for iron(III) ions was found to be 80.28 and 83.21%, respectively (Table 2), whereas in case of copper(II) ions, the efficiency of complexation was 82.28 and 82.40% with unsupported and polymer supported Schiff base.

The efficiency of complexation of zinc(II) ions on unsupported and polymer supported HPHZ Schiff base has varied from 81.51 to 83.17%, which indicated that zinc(II) ions were having more affinity for complexation with polymer supported HPHZ Schiff base in comparison to complexation efficiency of copper(II) ions (Table 2). These results have clearly suggested that the complexation of metal ions on polymer anchored HPHZ Schiff base was high in comparison to unsupported HPHZ Schiff base. The IR spectra of metal ions loaded Schiff base were recorded (Fig. 4), which showed significant variations in absorption bands corresponding to >C=N and >C–N functional groups of HPHZ Schiff base on complexation with metal ions. The appearance of new absorptions bands on complexation of metal ions was due to the formation of M–O and M–N bonds in HPHZ Schiff base complexes (Fig. 4).

The disappearance of phenolic absorption band (–C–OH) of HPHZ Schiff base has further provided an evidence for complexation of metal ions with HPHZ Schiff base. The absorption bands in polymer supported HPHZ Schiff base (Fig. 4A) appeared at low frequency in comparison to unsupported HPHZ Schiff base (Fig. 2A). On complexation of iron(III) ions with unsupported HPHZ Schiff base has shown absorption band at

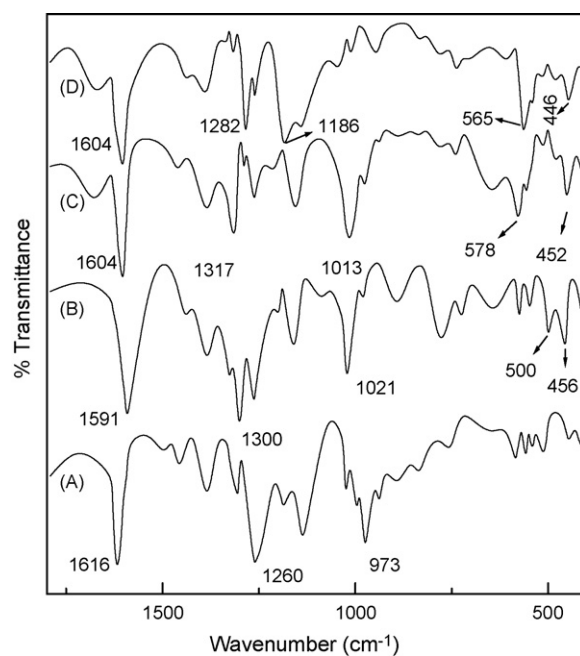


Fig. 4. FTIR spectra of polymer supported HPHZ Schiff base (A) and its metal complexes (B–D).

1595  $\text{cm}^{-1}$  corresponding to >C=N group, whereas absorption band in polymer supported HPHZ Schiff base was appeared at 1591  $\text{cm}^{-1}$  (Fig. 4A and B). Complexation of copper(II) and zinc(II) ions with unsupported and polymer supported HPHZ Schiff base shown absorption bands at 1608 and 1616  $\text{cm}^{-1}$  (Fig. 4C and D) corresponding to >C=N group of HPHZ Schiff base. These variations in absorption band for >C=N group was indicative that metal ions in these complexes interacted with azomethyne nitrogen of HPHZ Schiff base and appearance of absorption band at 465  $\text{cm}^{-1}$  with unsupported HPHZ Schiff base and at 456  $\text{cm}^{-1}$  with polymer supported HPHZ Schiff base has supported the formation of M–N bond by iron(III) ions with azomethyne nitrogen (Fig. 4B), but in case of copper(II) ions these bands appeared at 456 and 452  $\text{cm}^{-1}$  (Fig. 4C) and zinc(II) ions showed these bands at 452 and 447  $\text{cm}^{-1}$  (Fig. 4D) due to the formation of M–N bond by metal ions in unsupported and supported HPHZ, respectively. The complexation of iron(III), copper(II) and zinc(II) ions with polymer supported HPHZ Schiff base produced another absorption bands at 500  $\text{cm}^{-1}$  (Fig. 4B), 578  $\text{cm}^{-1}$  (Fig. 4C) and 565  $\text{cm}^{-1}$  (Fig. 4D), respectively, due to the formation of –O–M bond between metal ions and phenolic oxygen. Similar bands were shown by unsupported HPHZ Schiff base on complexation of these metal ions.

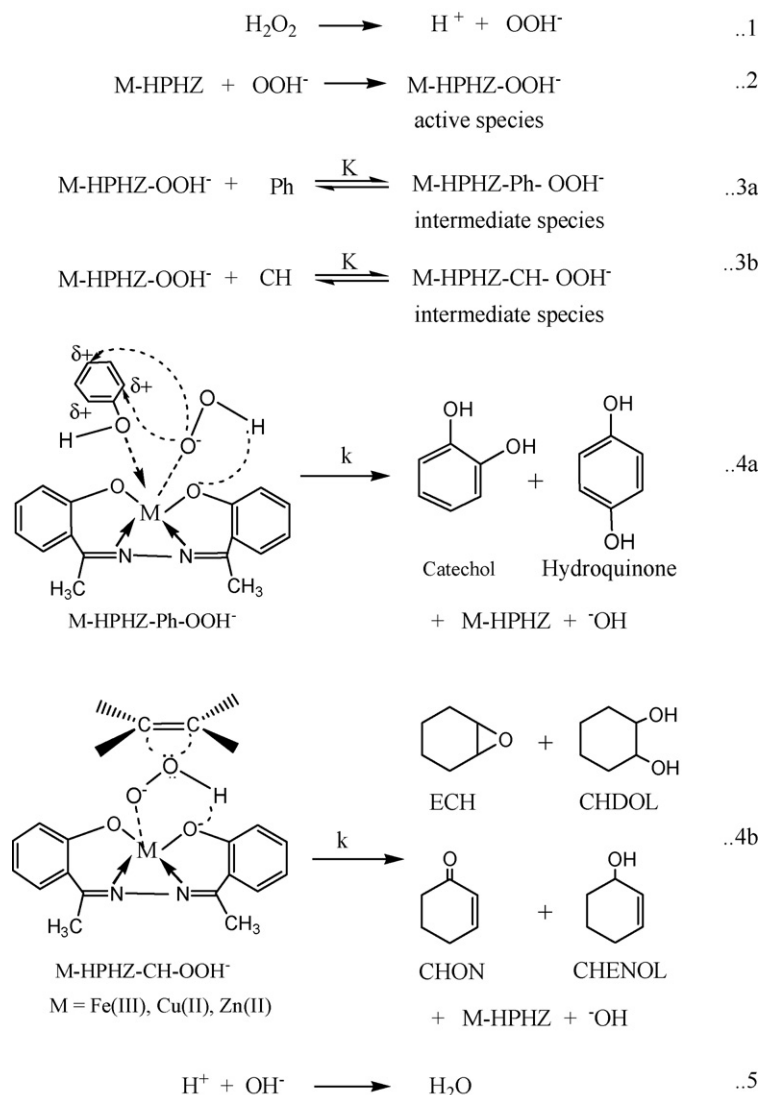
The complexation of metal ions with HPHZ Schiff base was further confirmed by comparing the electronic spectra of HPHZ Schiff base complexes of metal ions with electronic spectra of pure HPHZ Schiff base (Fig. 2). The complexation of iron(III) ions with HPHZ Schiff base showed variation in  $\pi \rightarrow \pi^*$  transitions from 219 to 285 nm and  $\pi \rightarrow \pi^*$  transitions in Schiff base complexes of copper(II) and zinc(II) ions appeared at 238 and 233 nm, respectively. On complexation of iron(III) ions, the  $n \rightarrow \pi^*$  transitions of HPHZ Schiff base was changed from

317 to 285 nm, whereas  $n \rightarrow \pi^*$  transitions appeared at 277 and 293 nm on complexation with copper(II) and zinc(II) ions, respectively. These  $C \rightarrow T$  and  $d \rightarrow d$  transitions were used as evidences for the complexation of metal ions with HPHZ Schiff base. The complexation of copper(II) ions with HPHZ Schiff base showed  $C \rightarrow T$  transition at 407 nm [47], but no  $C \rightarrow T$  transition was observed on complexation of iron(III) and copper(II) ions with HPHZ Schiff base. The complexation of iron(III) and copper(II) ions with HPHZ Schiff base showed  $d \rightarrow d$  transitions at 449 nm [48] and 570 nm [49], respectively, which clearly suggested for  $t_{2g}^5 e_g^0$ ,  $t_{2g}^6 e_g^3$  and  $t_{2g}^6 e_g^4$  electronic configurations for iron(III), copper(II) and zinc(II) ions in HPHZ Schiff base complexes. The magnetic moment ( $\mu$ ) of HPHZ Schiff base complexes of iron(III), copper(II) and zinc(II) ions was 1.73, 1.73 and 0.0 BM, respectively, which indicated that iron(III) and copper(II) ions complexes were paramagnetic with one unpaired electron in each and zinc(II) ions complexes were diamagnetic with all paired electrons. The elemental analysis, magnetic

moment ( $\mu$ ) and electronic state of metal ions in these complexes have suggested octahedral geometry ( $d^2sp^3$ ) for iron(III) ions complexes and square planar geometry ( $dsp^2$ ) for copper(II) ions complexes. The zinc(II) ions complexes showed tetrahedral ( $sp^3$ ) geometry.

### 3.4. Oxidation of phenol and epoxidation of cyclohexene

Catalytic activity of unsupported and polymer supported HPHZ Schiff base complexes of metal ions was evaluated by studying the oxidation of phenol and epoxidation of cyclohexene in presence of hydrogen peroxide as oxidant. The product identification and conversion of phenol and cyclohexene was studied using gas chromatographic technique. Catechol (CTL) and epoxy cyclohexane (ECH) were the major products in oxidation of phenol and epoxidation of cyclohexene (Scheme 3). The formation of reaction products in oxidation of phenol and epoxidation of cyclohexene has been attributed to the enzymatic behavior [50,51] of metal complexes of HPHZ Schiff base



Scheme 3. Oxidation of phenol and epoxidation of cyclohexene.

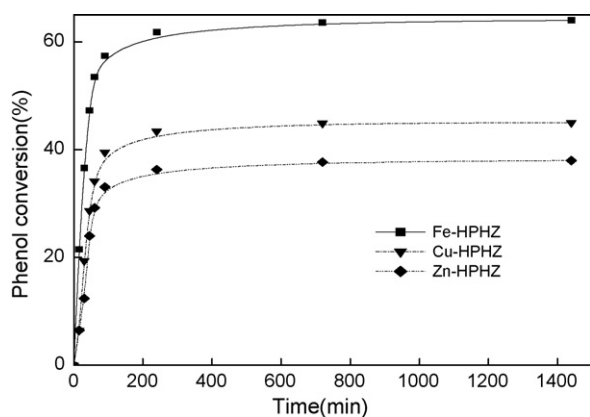


Fig. 5. Effect of reaction time on oxidation of phenol in presence of polymer supported metal complexes. [Phenol]:[catalyst]:[H<sub>2</sub>O<sub>2</sub>] = 1:1:1, temperature = 70 °C.

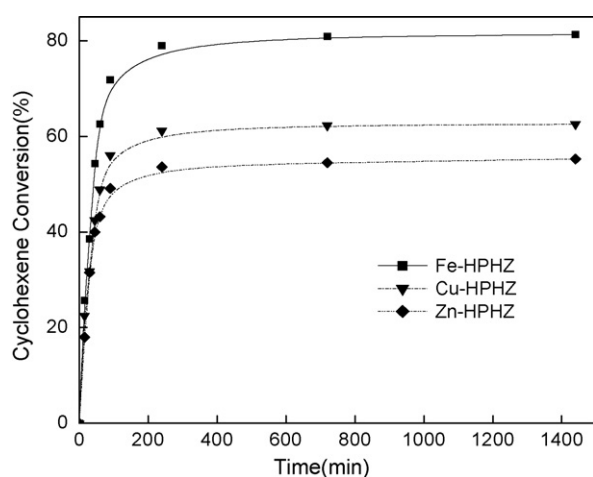


Fig. 6. Effect of reaction time on epoxidation of cyclohexene in presence of polymer supported metal complexes. [Cyclohexene]:[catalyst]:[H<sub>2</sub>O<sub>2</sub>] = 1:1:1, temperature = 40 °C.

(M-HPHZ), which produced initially an active species (M-HPHZ-OOH<sup>-</sup>) by the interactions of hydrogen peroxide (Scheme 3). The peroxyanions (OOH<sup>-</sup>) produced in step 1 are linked through d<sup>2</sup>sp<sup>3</sup> and dsp<sup>2</sup> orbital in HPHZ Schiff base complexes of iron(III) and copper(II) ions, respectively, and through sp<sup>3</sup> orbital in HPHZ Schiff base complexes of zinc(II) ions to produce the active species through a fast reaction [52,53]. The subsequent interactions of active species with phenol (Ph) and cyclohexene (CH) have produced intermediates (M-HPHZ-Ph-OOH<sup>-</sup> and M-HPHZ-CH-OOH<sup>-</sup>) through fast dynamic equilibrium [53]. The rate of electron exchange in the intermediate and its decomposition through a slow reaction step (*k*) has controlled the selective formation of catechol (CTL) in oxidation of phenol (Scheme 3) and epoxy cyclohexane (ECH) in epoxidation of cyclohexene (Scheme 3). The oxidation of phenol and epoxidation of cyclohexene was more prominent with polymer supported metal complexes (Figs. 5 and 6) in comparison to unsupported metal complexes (Table 3).

The high catalytic activity of polymer supported HPHZ Schiff base complexes of metal ions was due to the better control of metal ions interactions with substrate in the intermediates in comparison to the intermediates of unsupported metal complexes. The low activity of unsupported metal complexes was due to the formation of dimers or multimers by the catalyst in the solution. The polymer support might have assisted in exchange of electron in the intermediate (M-HPHZ-Ph-OOH<sup>-</sup> and M-HPHZ-CH-OOH<sup>-</sup>) as well as in decomposition of the intermediate to facilitate the formation of reaction product through an easiest route of energy surfaces in comparison to unsupported Schiff base complexes. The oxidation products of phenol showed separation peaks corresponding to catechol and hydroquinone in the chromatogram; hence, the formation of polyphenols in the oxidation of phenol was discarded.

The oxidation of cyclohexene in presence of HPHZ Schiff base complexes of metal ions has produced epoxy cyclohexane as major product (ECH) and 1,2-cyclohexanediol (CHDOL), 2-cyclohexene-1-one (CHON), 2-cyclohexene-1-ol (CHENOL) as minor products (Scheme 3). The oxidation of phenol (Ph) and epoxidation of cyclohexene (CH) with unsupported (Table 3) and supported Schiff base complexes of iron(III), copper(II) and zinc(II) ions (Figs. 5 and 6) was initially fast upto 6 h and then after it was almost constant. These reactions also varied with type of the catalyst (Table 3 and Figs. 5 and 6). The percent conversion of phenol and cyclohexene was more with polymer supported Schiff base complexes of iron(III) in comparison to copper(II) and zinc(II) ions complexes (Figs. 5 and 6). The catalytic activity of supported catalysts was almost constant up to six recycles and then after it decreased without any significant variation in product selectivity (Table 4), which indicated clearly that the structures of metal complexes on polymer support remained almost same upto six recycles. This was further confirmed by comparing the IR spectra of recycled Schiff base complexes of metal ions with IR spectra of freshly prepared supported metal complexes.

The catalytic activity of HPHZ Schiff base complexes of metal ions in oxidation of phenol and epoxidation of cyclohexene was also evaluated taking different molarity of phenol,

Table 3

Catalytic activity of unsupported metal complexes (M-HPHZ) in oxidation of phenol (pH) and epoxidation of cyclohexene (CH)

Time (min)	Percent conversion					
	Fe-HPHZ		Cu-HPHZ		Zn-HPHZ	
	Ph	CH	Ph	CH	Ph	CH
0	0.0	0.0	0.0	0.0	0.0	0.0
15	7.9	14.9	3.4	9.6	1.5	5.6
30	17.5	26.0	9.0	16.6	3.5	10.6
45	27.2	36.4	20.8	30.7	7.8	18.1
60	34.4	43.7	27.4	36.8	12.4	23.8
90	40.7	53.4	33.7	46.0	14.7	30.5
240	48.0	63.6	37.2	53.8	18.0	37.3
720	50.0	65.2	38.4	55.2	18.6	39.3
1440	50.5	66.4	39.3	55.6	19.2	39.9

[H<sub>2</sub>O<sub>2</sub>]/[catalyst]/[Ph]/[CH] = 0.05 M, temperature = 70 °C (Ph), 40 °C (CH).



Table 4

Efficiency of recycled supported catalysts (P-HPHZ-M) in oxidation of phenol and epoxidation cyclohexene

Cycle number	P-HPHZ-Fe	P-HPHZ-Cu	P-HPHZ-Zn
Conversion of phenol (%)			
2	64.0	45.0	38.0
4	64.0	45.0	37.6
6	63.8	44.8	37.2
8	55.0	37.2	29.2
10	48.3	30.2	20.8
Conversion of cyclohexene (%)			
2	81.3	62.6	55.3
4	81.1	62.6	55.2
6	81.0	62.1	54.8
8	75.8	55.2	43.2
10	60.2	43.2	30.8

[H<sub>2</sub>O<sub>2</sub>]/[Ph]/[CH] = 0.05 M, time = 1440 min, temperature = 70 °C (Ph), 40 °C (CH), CH<sub>3</sub>CN = 2.0 mL.

cyclohexene and hydrogen peroxide in the reaction mixture and variation in product and product selectivity was determined.

### 3.4.1. Effect of H<sub>2</sub>O<sub>2</sub> concentration on oxidation of phenol and epoxidation of cyclohexene

The effect of H<sub>2</sub>O<sub>2</sub> concentration on oxidation of phenol and epoxidation of cyclohexene was studied by varying the molar ratio of H<sub>2</sub>O<sub>2</sub> to phenol from 0.5 to 2.0 at constant molarity of phenol/cyclohexene and catalyst (0.05 M) in the reaction mixture. The epoxidation of cyclohexene was carried out at 40 °C and oxidation of phenol at 70 °C. On increasing the molar ratio of hydrogen peroxide from 0.5 to 1.0 at constant molar ratio of phenol/cyclohexene and catalysts, the conversion of phenol and cyclohexene increased in presence of HPHZ Schiff base complexes of iron(III), copper(II) and zinc(II) ions (Figs. 7 and 8), but on further increasing the molar ratio of H<sub>2</sub>O<sub>2</sub> (>1), the percent conversion of phenol and cyclohexene decreased both with unsupported and supported HPHZ Schiff base complexes of iron(III), copper(II) and zinc(II) ions. The decreasing trend in percent conversion of phenol and cyclohexene at high molar ratio of hydrogen peroxide (>1) was attributed to the decrease in molar

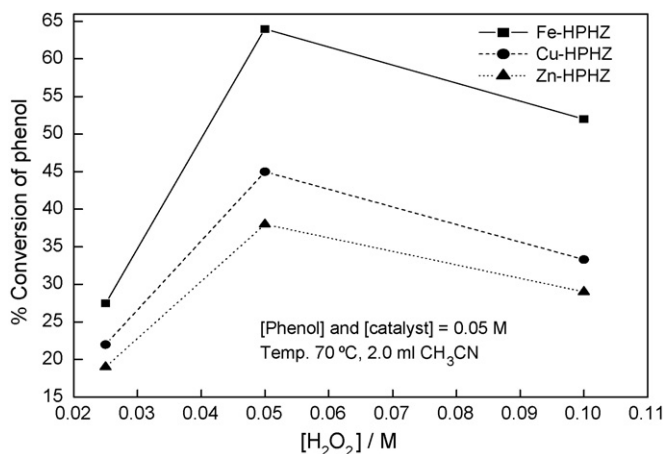


Fig. 7. Effect of H<sub>2</sub>O<sub>2</sub> concentration on phenol conversion. [Phenol]:[catalyst] = 1:1, temperature = 70 °C.

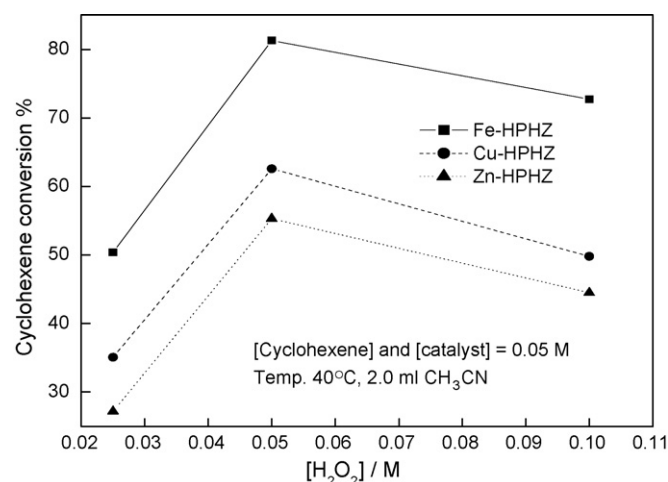


Fig. 8. Effect of H<sub>2</sub>O<sub>2</sub> concentration on phenol conversion. [Cyclohexene]:[catalyst] = 1:1, temperature = 40 °C.

ratio of phenol/cyclohexene and catalyst than the molar ratio of H<sub>2</sub>O<sub>2</sub>. The phenol and cyclohexene conversion was maximum with HPHZ Schiff base complexes of iron(III) ions and lowest with HPHZ Schiff base complexes of zinc(II) ions. On varying the molar ratio of hydrogen peroxide, the product selectivity for catechol (CTL) and epoxy cyclohexane (ECH) remained almost constant. The average selectivity for catechol (CTL) was around 90 wt% with Schiff base complexes of iron(III) ions and 86 wt% with Schiff base complexes of zinc(II) ions. Similarly, the average selectivity for epoxy cyclohexane (ECH) with Schiff base complexes of iron(III) ions was 96.5 and 87.5 wt% with Schiff base complexes of zinc(II) ions. The selectivity for epoxy cyclohexane was more with all metal ions in comparison to selectivity for catechol in oxidation of phenol, which has clearly indicated that polymer supported HPHZ Schiff base complexes were more efficient in catalyzing the epoxidation of cyclohexene in comparison to oxidation of phenol.

The rate of phenol oxidation was maximum ( $2.13 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) with Schiff base complex of iron(III) ions than Schiff base complexes of copper(II) and zinc(II) ions in which the rate of phenol oxidation was  $1.51 \times 10^{-6}$  and  $1.26 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ , respectively, at optimum molar ratio of 1:1:1 of H<sub>2</sub>O<sub>2</sub> to phenol and catalyst, but rate of phenol oxidation and product selectivity was lowest with unsupported Schiff base complexes of metal ions at same molar ratio of reactants. The turn over number (TON) for oxidation of phenol was highest ( $14.82 \text{ g mol}^{-1} \text{ Fe h}^{-1}$ ) in presence of supported Schiff base complexes of iron(III) ions than Schiff base complexes of copper(II) ( $10.20 \text{ g mol}^{-1} \text{ Cu h}^{-1}$ ) and zinc(II) ions ( $8.53 \text{ g mol}^{-1} \text{ Zn h}^{-1}$ ) at optimum molar ratio of reactants. The rate (R<sub>p</sub>) of epoxidation of cyclohexene was maximum at ( $2.74 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) with supported Schiff base complexes of iron(III) ions and lowest with unsupported Schiff base complexes of iron(III) ions. The turn over number (TON) for unsupported and supported Schiff base complexes of metal ions in epoxidation of cyclohexene was highest than turn over number shown by Schiff base complexes of metal ions in oxidation of phenol.

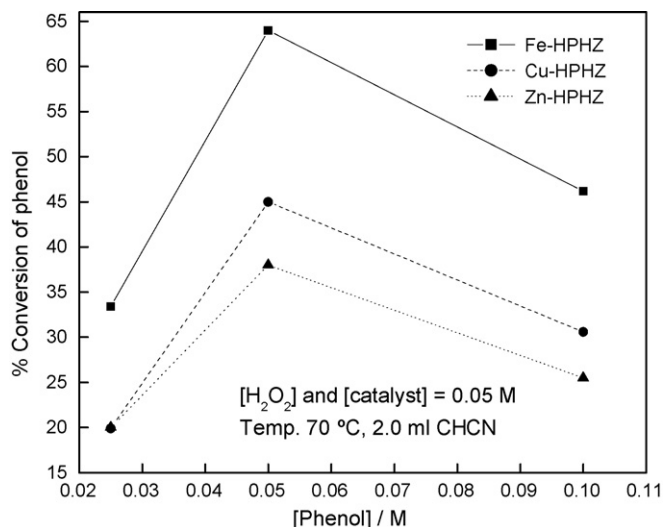


Fig. 9. Effect of concentration of phenol on its oxidation.  $[H_2O_2]:[catalyst] = 1:1$ , temperature =  $70^\circ C$ .

### 3.4.2. Effect of substrate concentration on oxidation and epoxidation

The efficiency of catalysts in oxidation of phenol and in epoxidation of cyclohexene was also evaluated at different molar ratios of phenol and cyclohexene at constant molarity of hydrogen peroxide and catalyst (0.05 M). The molar ratio of phenol and cyclohexene varied from 0.5 to 2.0 than the molar ratio of hydrogen peroxide and catalyst. The oxidation of phenol and epoxidation of cyclohexene increased with the increase in molar ratio of phenol and cyclohexene from 0.5 to 1.0 (Figs. 9 and 10), but on further increasing the molar ratio of phenol and cyclohexene, the conversion of phenol and cyclohexene decreased (Figs. 9 and 10). The decreasing trend in oxidation of phenol and epoxidation of cyclohexene at high molar ratio ( $>1$ ) of substrate was due to the decrease in molar ratio of oxidant and catalyst in the reaction mixture. The oxidation of phenol and epoxidation of cyclohexene was maximum 1:1:1 molar ratio

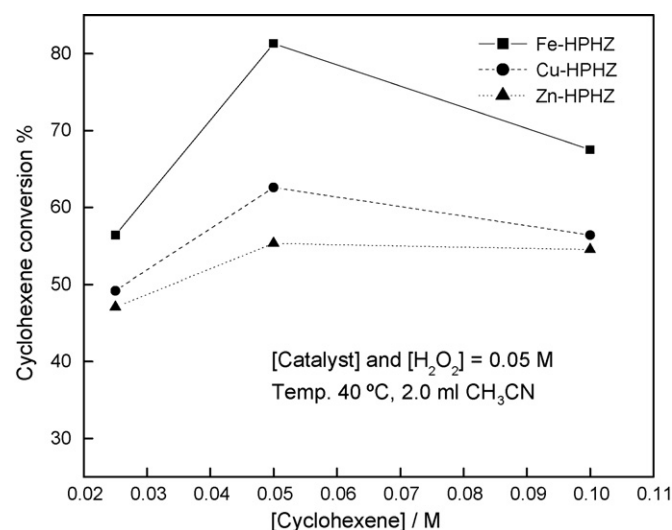


Fig. 10. Effect of concentration of cyclohexene on its oxidation.  $[H_2O_2]:[catalyst] = 1:1$ , temperature =  $40^\circ C$ .

Table 5

Effect of supported catalyst concentration on selectivity for catechol (CTL) and epoxy cyclohexane (ECH)

Molarity of catalyst (M)	Selectivity for catechol (CTL)	Selectivity forepoxy cyclohexane (ECH)
P-HPHZ-Fe		
0.025	87.2	92.8
0.050	90.5	96.5
0.100	89.2	95.1
P-HPHZ-Cu		
0.025	84.1	87.8
0.050	88.8	91.2
0.100	86.4	89.8
P-HPHZ-Zn		
0.025	82.5	85.6
0.050	86.1	87.6
0.100	85.3	87.1

$[H_2O_2]/[Ph]/[CH] = 0.05 M$ , time = 1440 min, temperature =  $70^\circ C$  (Ph),  $40^\circ C$  (CH),  $CH_3CN = 2.0 mL$ .

of phenol/cyclohexene to hydrogen peroxide and catalyst. The selectivity for catechol was constant on varying the molar ratio of phenol and was maximum with Schiff base complexes of iron(III) ions than Schiff base complexes of copper(II) and zinc(II) ions. Similar trend in selectivity for epoxy cyclohexane was observed in epoxidation of cyclohexene, which has indicated that the activity of catalyst remained constant on varying the molar ratio of phenol and cyclohexene in the reaction mixtures (Table 5).

Rate of phenol oxidation and epoxidation of cyclohexene has increased on increasing the molar ratio of phenol/cyclohexene from 0.5 to 1.0 at constant molar ratio of hydrogen peroxide and catalyst.

The rate of oxidation of phenol ( $2.13 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) and epoxidation of cyclohexene ( $2.74 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) was maximum at 1:1:1 molar ratio of phenol/cyclohexene with  $H_2O_2$  and catalyst and with Schiff base complexes of iron(III) ions than Schiff base complexes of other metal ions. Turn over number (TON) was increased on increasing the molar ratio of phenol/cyclohexene in the reaction mixture and was maximum at 1:1:1 molar ratio of phenol/cyclohexene to hydrogen peroxide and catalyst. In both reactions, the turn over number was maximum with Schiff base complexes of iron(III) ions and the value of turn over number (TON) was comparatively more in epoxidation of cyclohexene than in oxidation of phenol, which was an indicative for high activity of Schiff base complexes in epoxidation of cyclohexene than oxidation of phenol. The recyclability of Schiff base complexes in epoxidation of cyclohexene was more than Schiff base complexes used in oxidation of phenol (Table 4).

### 3.4.3. Effect of concentration of catalysts in oxidation of phenol and epoxidation of cyclohexene

Effect of molar ratio of catalysts in oxidation of phenol and epoxidation of cyclohexene was evaluated using different molar ratios of catalysts in comparison to oxidant and substrate. The molar ratio of Schiff base complexes of iron(III), copper(II) and

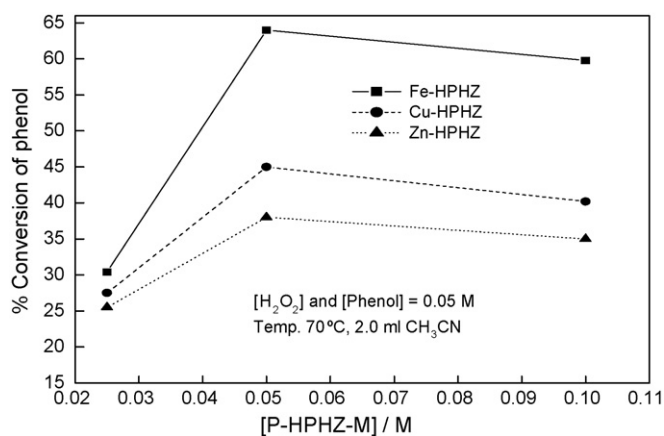


Fig. 11. Effect of supported catalyst concentration on oxidation of phenol. [Phenol]:[H<sub>2</sub>O<sub>2</sub>] = 1:1, temperature = 70 °C.

zinc(II) ions has varied from 0.5 to 2.0 at constant molarity (0.05 M) of phenol/cyclohexene and hydrogen peroxide in the reaction mixture. The oxidation of phenol was studied at 70 °C and epoxidation of cyclohexene at 40 °C. On increasing the molar ratio of Schiff base complexes of iron(III) ions from 0.5 to 1.0, the oxidation of phenol and epoxidation of cyclohexene was increased and showed 64 wt% oxidation of phenol and 81.3 wt% epoxidation of cyclohexene at 1:1:1 molar ratio of catalysts with hydrogen peroxide and phenol/cyclohexene (Figs. 11 and 12).

The Schiff base complexes of copper(II) and zinc(II) ions also showed highest conversion of phenol and epoxidation of cyclohexene at 1:1:1 molar ratio of catalyst to hydrogen peroxide and substrates (Figs. 11 and 12). On further increasing the molar ratio of Schiff base complexes of metal ions (>1), the oxidation of phenol and epoxidation of cyclohexene has shown decreasing trend (Figs. 11 and 12), which was due to the decrease in molar ratio of phenol/cyclohexene (<1) in comparison to the molar ratio of catalysts. The low activity at low molar ratio of catalyst (<1) to phenol/cyclohexene and hydrogen peroxide was due to insufficient amount of catalysts in comparison to phenol/cyclohexene and hydrogen peroxide in the reaction mixture (Figs. 11 and 12). These results have clearly indicated that the

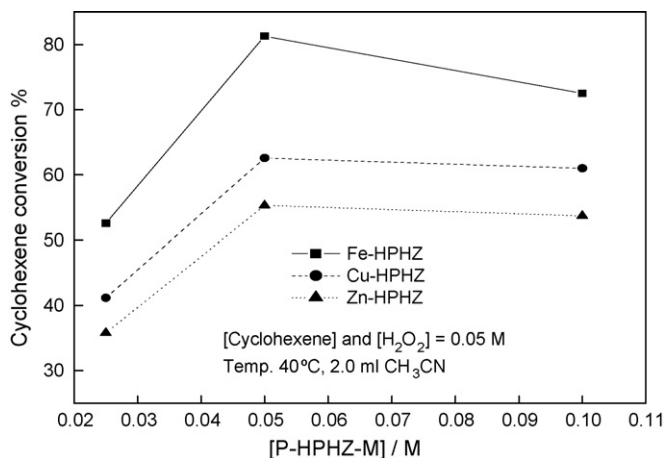


Fig. 12. Effect of supported catalyst concentration on epoxidation of cyclohexene. [Cyclohexene]:[H<sub>2</sub>O<sub>2</sub>] = 1:1, temperature = 40 °C.

oxidation of phenol and epoxidation of cyclohexene was maximum at 1:1:1 molar ratio of catalyst to phenol/cyclohexene and hydrogen peroxide. The molar ratio of catalyst has influenced the selectivity for catechol in oxidation of phenol and epoxy cyclohexane in epoxidation of cyclohexene (Table 5).

Product selectivity has decreased at high molar ratio of catalysts (>1), which was attributed for significant variation in microenvironment on active sites of the catalyst. The interactions of phenol and cyclohexene in peroxo intermediates (M-HPHZ-Ph-OOH<sup>-</sup> and M-HPHZ-CH-OOH<sup>-</sup>) were affected seriously at high molar ratio of catalyst in the reaction mixture (Scheme 3); hence, the conversion and product selectivity decreased at high molar ratio (>1) of the catalysts. The product selectivity remained constant during molar ratio variation of hydrogen peroxide and substrates, which indicated clearly that the interactions of substrates with catalyst in the intermediates (M-HPHZ-Ph-OOH<sup>-</sup> and M-HPHZ-CH-OOH<sup>-</sup>) remained constant during molar ratio variation of hydrogen peroxide and substrates. The rate of oxidation of phenol and epoxidation of cyclohexene with unsupported Schiff base complexes of iron(III) ions was  $1.97 \times 10^{-6}$  and  $2.5 \times 10^{-6}$  mol dm<sup>-3</sup> s<sup>-1</sup>, respectively, whereas, with supported Schiff base complexes of iron(III) ions, the rate for oxidation of phenol and epoxidation of cyclohexene was  $2.13 \times 10^{-6}$  and  $2.74 \times 10^{-6}$  mol dm<sup>-3</sup> s<sup>-1</sup>, respectively, which indicated clearly that the activity of catalyst was influenced by polymer support. The rate of oxidation of phenol and epoxidation of cyclohexene was also high with supported Schiff base complexes of copper(II) and zinc(II) ions than unsupported Schiff base complexes. The turn over number (TON) at different molar ratios of catalyst was also determined and found to be optimum at 1:1:1 molar ratios of unsupported and supported catalysts.

#### 3.4.4. Effect of reaction temperature on oxidation of phenol and epoxidation of cyclohexene

To determine the energy of activation for oxidation of phenol and epoxidation of cyclohexene, the studies also carried out at different temperatures. The temperature was varied from 60 to 80 °C in oxidation of phenol and from 30 to 50 °C in epoxidation of cyclohexene at 1:1:1 molar ratio of phenol/cyclohexene to catalyst and hydrogen peroxide at 0.05 molarity of the reactants. The energy of activation was calculated using rate constant (*k*) determined at different temperatures. The oxidation of phenol and epoxidation of cyclohexene increased on increasing the reaction temperature from 60 to 70 °C and 30 to 40 °C, respectively (Table 6), but on increasing the temperature beyond 70 °C in oxidation of phenol and 40 °C in epoxidation of cyclohexene, the oxidation of phenol and epoxidation of cyclohexene was decreased. The decreasing trend in oxidation of phenol at high temperature (>70 °C) was attributed to the decomposition of hydrogen peroxide without oxidizing the phenol and also due to the variation in microenvironment in intermediate of the catalysts, but decreasing effect of temperature (>40 °C) in epoxidation of cyclohexene was purely due to the variation in microenvironment in the intermediate of the catalysts on polymer support.

Table 6

Effect of temperature on conversion of phenol (Ph)/cyclohexene (CH) and product selectivity with supported Schiff base complexes of metal ions (P-HPHZ-M)

Temperature (°C)	Ph-conversion (%) and CTL-selectivity (%)					
	P-HPHZ-Fe		P-HPHZ-Cu		P-HPHZ-Zn	
	Ph	CTL	Ph	CTL	Ph	CTL
60	42.1	86.1	31.5	83.2	29.5	80.0
70	64.0	90.5	45.0	88.8	38.0	86.1
80	61.4	88.2	42.4	85.7	34.9	82.5

Temperature (°C)	CH conversion (%) and ECH selectivity (%)					
	P-HPHZ-Fe		P-HPHZ-Cu		P-HPHZ-Zn	
	CH	ECH	CH	ECH	CH	ECH
30	66.4	92.7	42.6	85.8	38.6	83.1
40	81.3	96.5	62.6	91.2	55.3	87.1
50	79.4	94.9	59.9	88.3	51.7	84.6

[H<sub>2</sub>O<sub>2</sub>]/[catalyst]/[Ph]/[CH] = 0.05 M, time = 1440 min, CH<sub>3</sub>CN = 2.0 mL.

The variation in interactions of substrate with catalyst and microenvironment at high temperature has influenced the product selectivity for catechol (CTL) and epoxy cyclohexane (ECH) (Table 6). The selectivity for catechol in oxidation of phenol was maximum at 70 °C and for epoxy cyclohexane (ECH) in epoxidation of cyclohexene at 40 °C. The rate constant (*k*) for oxidation of phenol with supported and unsupported Schiff base complexes of iron(III) ions was  $4.29 \times 10^{-5}$  and  $3.54 \times 10^{-5} \text{ s}^{-1}$ , respectively, at 70 °C. Similarly the rate constant (*k*) for epoxidation of cyclohexene with supported and unsupported Schiff base complexes of iron(III) ions was

$5.49 \times 10^{-5}$  and  $5.0 \times 10^{-5} \text{ s}^{-1}$ , respectively, at 40 °C, which clearly indicated that rate constants were higher with supported catalysts and varied with type of metal ions in Schiff base complexes. The rate constants (*k*) showed significant variation with reaction temperature, which clearly indicated that oxidation and epoxidation reactions were energy activated processes and polymer support has played a significant role in reducing the energy of activation. The energy of activation for oxidation of phenol and epoxidation of cyclohexene for different catalysts is shown in Tables 7 and 8. The energy of activation for oxidation of phenol (22.8 kJ mol<sup>-1</sup>) and epoxidation of cyclohexene (8.9 kJ mol<sup>-1</sup>) was low in presence of Schiff base complexes of iron(III) ions than Schiff base complexes of copper(II) and zinc(II) ions. The activation energy for oxidation of phenol (23.1 kJ mol<sup>-1</sup>) and epoxidation of cyclohexene (11.6 kJ mol<sup>-1</sup>) with unsupported Schiff base complexes of iron(III) ions was high and same trend was observed with Schiff base complexes of copper(II) and zinc(II) ions (Table 7), which indicated clearly that polymer support was useful in reduction of energy of activation in oxidation of phenol and epoxidation of cyclohexene. Although energy of activation for oxidation of phenol with Schiff base complexes of zinc(II) ions was low than Schiff base complexes of copper(II) ions, but percent conversion and product selectivity in oxidation of phenol and epoxidation of cyclohexene was lower than Schiff base complexes of copper(II) ions, which might be attributed to the difference in electronic configuration and geometry of Schiff base complexes of zinc(II) ions than Schiff base complexes of iron(III) and copper(II) ions.

The difference in geometry and electronic state was responsible to control the interactions of phenol and cyclohexene

Table 7

Kinetic parameters for oxidation of phenol and selectivity for catechol (CTL)

Catalysts	Conversion (%)	Selectivity (%)	Rp ( $\times 10^6 \text{ ML}^{-1} \text{ s}^{-1}$ )	TON ( $\text{g mol M}^{-1} \text{ h}^{-1}$ )	E <sub>a</sub> (kJ mol <sup>-1</sup> )
With unsupported catalysts (HPHZ-M)					
HPHZ-Fe	56.0	86.0	1.94	13.13	23.1
HPHZ-Cu	38.2	82.0	1.33	8.97	42.4
HPHZ-Zn	31.6	78.0	1.10	7.43	38.4
With supported catalysts (P-HPHZ-M)					
P-HPHZ-Fe	61.8	90.5	2.13	14.82	22.8
P-HPHZ-Cu	43.4	88.8	1.51	10.20	39.7
P-HPHZ-Zn	36.3	86.1	1.26	8.53	28.9

[H<sub>2</sub>O<sub>2</sub>]/[catalyst]/[phenol] = 0.05 M, time = 1440 min, CH<sub>3</sub>CN = 2.0 mL.

Table 8

Kinetic parameters for epoxidation of cyclohexene and selectivity for epoxy cyclohexane (ECH)

Catalysts	Conversion (%)	Selectivity (%)	Rp ( $\times 10^6 \text{ ML}^{-1} \text{ s}^{-1}$ )	TON ( $\text{g mol M}^{-1} \text{ h}^{-1}$ )	E <sub>a</sub> (kJ mol <sup>-1</sup> )
With unsupported catalysts (HPHZ-M)					
HPHZ-Fe	72.0	92.0	2.50	14.76	11.6
HPHZ-Cu	54.5	89.0	1.89	11.17	16.6
HPHZ-Zn	47.8	82.0	1.65	9.80	35.9
With supported catalysts (P-HPHZ-M)					
P-HPHZ-Fe	79.0	96.5	2.74	16.20	8.9
P-HPHZ-Cu	61.2	91.2	2.13	12.55	15.2
P-HPHZ-Zn	53.6	87.1	1.86	10.98	33.5

[H<sub>2</sub>O<sub>2</sub>]/[catalyst]/[cyclohexene] = 0.05 M, time = 1440 min, CH<sub>3</sub>CN = 2.0 mL.

in peroxo intermediates ( $M\text{-HPHZ-Ph-OOH}^-$  and  $M\text{-HPHZ-CH-OOH}^-$ ). The percent conversion of phenol/cyclohexene and turn over number for supported and unsupported Schiff base complexes of iron(III), copper(II) and zinc(II) ions are shown in Tables 7 and 8, which clearly indicated that polymer supported Schiff base complexes were more efficient catalysts than unsupported Schiff base complexes of metal ions.

#### 4. Conclusions

Polymer supported metal complexes of  $N,N'$ -bis (*o*-hydroxy acetophenone) hydrazine (HPHZ) Schiff base were synthesized successfully by anchoring  $N,N'$ -bis (4-amino-*o*-hydroxy acetophenone) hydrazine Schiff base (AHPHZ) on polymer beads. The unsupported and polymer supported HPHZ Schiff base complexes of metal ions were characterized for structures by spectral and magnetic measurements. The activity of unsupported and polymer supported Schiff base complexes of metal ions was evaluated by studying the oxidation of phenol and epoxidation of cyclohexene in presence of hydrogen peroxide as oxidant. Amongst the various metal ions, the activity of Schiff base complexes of iron(III) ions was higher than Schiff base complexes of copper(II) and zinc(II) ions. The product selectivity for catechol and epoxy cyclohexane showed dependence on polymer support and type of catalyst. The effect of various experimental conditions was also studied and a suitable mechanism and reactions steps are proposed for oxidation of phenol and epoxidation of cyclohexene. The polymer support has played a significant role in decreasing the energy of activation for oxidation of phenol and epoxidation of cyclohexene in presence of Schiff base complexes of iron(III), copper(II) and zinc(III) ions, which were used as catalysts.

#### Acknowledgements

Authors are thankful to I.I.T. Roorkee for providing research facilities. One of the authors Mr. A.K. Sutar is thankful to MHRD New Delhi, Government of India for the award of fellowship.

#### References

- [1] T. Mukaiyama, T. Yamada, Bull. Chem. Soc. Jpn. 68 (1995) 17.
- [2] P. Mastroritte, C.F. Nobile, G.P. Suran, L. Lopez, Tetrahedron 51 (1995) 7943.
- [3] G.T. Musie, M. Wei, B. Subramaniam, D.H. Busch, Inorg. Chem. 40 (14) (2001) 3336–3341.
- [4] G.T. Musie, M. Wei, B. Subramaniam, D.H. Busch, Coord. Chem. Rev. 219–221 (2001) 789–820.
- [5] B. Andrea, S. Martino, C. Beniditto, J. Mol. Catal. A: Chem. 250 (2006) 1–5.
- [6] T. Shahram, H.M. Hossein, M. Valiollah, M. Mazid, G. Gholamhossein, Inorg. Chem. 9 (6) (2006) 575–578.
- [7] D.W. Yoo, J.H. Han, S.H. Nam, C. Kim, J.K. Lee, Inorg. Chem. Commun. 9 (2006) 654–657.
- [8] A. Akelah, A. Rehab, E.-R. Kenawy, Abou M.S. Zeid, J. Appl. Polym. Sci. 101 (2) (2006) 1121–1129.
- [9] B. Stefan, S. Agniesszker, S. Beata, Appl. Catal. A: Gen. 309 (2006) 85–90.
- [10] E. Blaz, J. Pielichowski, Molecules 11 (2006) 115–120.
- [11] B. Olivier, S. Thierry, T. Bruno, L. Govic, A. Marie, Fr. Demande 44 (2003) 65.
- [12] S. Liu, S. Huang, W. Xin, J. Bai, S. Xie, L. Xu, Catal. Today 93–95 (2004) 471–476.
- [13] C.H. Mônica, D. Jairton, C.S. Fernanda, J.H.Z. dos Santos, J. Mol. Catal. A: Chem. 197 (2003) 223–232.
- [14] A.C.A. Casagrande, T.T.R. Tavares, M.C.A. Kuhn, O.L. Casagrande, J.H.Z. dos Santos, T. Teranishi, J. Mol. Catal. A: Chem. 212 (2004) 267–275.
- [15] R.-M. Wang, Z.-L. Zhang, J.-F. Lou, Y.-P. Wang, P.-F. Song, C.-G. Xia, Polym. Adv. Technol. 15 (1/2) (2004) 48–51.
- [16] P. Liu, L. Wang, L.-M. Li, X.-Y. Wang, Youji Huaxue 24 (59) (2004) 62.
- [17] E. Brule, M. de, R. Yolanda, K.K. Hi, Tetrahedron 60 (2004) 5913–5918.
- [18] A. Zsigmond, K. Boger, F. Notheisz, J. Catal. 213 (2003) 103.
- [19] D. Gournis, M. Louludi, M.A. Karukassides, C. Kolokytha, K. Metopoupou, N. Hadjiliadis, Mater. Sci. Eng. C 22 (1) (2002) 113–116.
- [20] D.C. Sherrington, Catal. Today 57 (2000) 87.
- [21] A.R. Silva, J.L. Figueredo, C. Fieire, B. de Castro, Microporous Mesoporous Mater. 68 (2004) 83.
- [22] G.-J. Kim, D.-W. Park, Catal. Today 63 (2000) 537.
- [23] T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, Chem. Lett. (1991) 1.
- [24] Qu Yulong, Hu Daodao, Gaofenzi Tongbao 1 (2005) 31–37.
- [25] T. Shahram, H.M. Hossein, M.V. Moghadam, M.G. Gholamhossein, J. Mol. Catal. A: Chem. 255 (1/2) (2006) 249–253.
- [26] E.K. Beloglazkina, A.G. Majangu, R.B. Romashkima, N.V. Zyk, Tetrahedron Lett. 47 (17) (2006) 2957–2959.
- [27] K.C. Gupta, H.K. Abdulkadir, S. Chand, J. Mol. Catal. A: Chem. 202 (2003) 253–268.
- [28] I. Owsik, B.N. Kolarz, J. Jezierska, Catal. Lett. 107 (2006) 197–203.
- [29] W.A. Hermann, R.W. Fisher, W. Scherer, M.U. Ranch, Angew. Chem. 105 (1993) 1209.
- [30] W.A. Hermann, R.W. Fisher, D.W. Marz, Angew. Chem. 103 (1991) 1706.
- [31] M.M. Hashemi, Y.A. Bani, J. Chem. Res. (S) (1998) 138–139.
- [32] M.M. Miller, D.C. Sherrington, J. Catal. 152 (1995) 368.
- [33] G. Olason, D.C. Sherrington, React. Funct. Polym. 42 (1999) 163.
- [34] X. Kou, S. Cheng, J. Du, X. Yu, X. Zeng, J. Mol. Catal. A: Chem. 210 (2004) 23–29.
- [35] G.A. Morris, S.T. Nguyen, J.T. Hupp, J. Mol. Catal. A: Chem. 174 (2001) 15–20.
- [36] B.H. Huang, C.N. Lin, M.L. Hsueh, T. Athar, C.C. Lin, Polymer 47 (2006) 6622–6629.
- [37] H. Du, X. Zhang, Z. Wang, K. Ding, Tetrahedron 61 (2005) 9465–9477.
- [38] M.R. Kratz, D.G. Hendricker, Polymer 27 (1986) 1641.
- [39] Y. Vouzumi, T. Kimura, Synlett 12 (2002) 2045–2048.
- [40] I. Cazaux, C. Caze, Eur. Polym. J. 29 (1993) 1615.
- [41] K.C. Gupta, H.K. Abdulkadir, S. Chand, J. Macromol. Sci. Pure Appl. Chem. A 39 (2002) 1451–1474.
- [42] S.S. Gupta, P. Samudranil, Inorg. Chem. 44 (2005) 6299–6307.
- [43] A.I. Vogel, Textbook of Practical Organic Chemistry, ELBS and Longman, London, 1978.
- [44] L. Hankova, L. Holub, K. Jerabek, React. Funct. Polym. 66 (2006) 592–598.
- [45] J.W. Yoon, J.S. Chang, H.D. Lee, T.J. Kim, S.H. Jung, J. Mol. Catal. A: Chem. 260 (2006) 181–186.
- [46] B. Wang, H.Z. Ma, Inorg. Chem. Commun. 4 (2001) 248–251.
- [47] B.M. Weckhuysen, A.A. Verberckmoes, L. Fu, R.A. Schoonheydt, J. Phys. Chem. 100 (1996) 9456–9461.
- [48] A.B.P. Lever, S. Licoccia, B.S. Ramaswamy, Inorg. Chim. Acta 64 (1982) L87–L90.
- [49] S.N. Masoud, A. Ahmad, Appl. Catal. A: Gen. 290 (2005) 46–53.
- [50] S.X. Li, J.Z. Li, J.Q. Xie, Y. Chen, X.G. Meng, C.W. Hu, X.C. Zeng, Huaxue Xuebao 62 (2004) 567–572.
- [51] J.Q. Xie, J.Z. Li, X.G. Meng, C.W. Hu, X.C. Zeng, S.X. Li, Trans. Met. Chem. 29 (2004) 388–393.
- [52] F. Bigoli, B. Antonio, T. Antonio, T.C. Marisa, J. Chem. Soc. Section D, Chem. Commun. 2 (1970) 120.
- [53] R.L. Belford, Inorg. Chem. 8 (1969) 1312.