Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Gupta, K. C. and Sutar, A. K.(2007) 'Polymer Supported Schiff Base Complexes of Iron(III), Cobalt(II) and Nickel(II) Ions and their Catalytic Activity in Oxidation of Phenol and Cyclohexene', Journal of Macromolecular Science, Part A, 44: 11, 1171 — 1185

To link to this Article: DOI: 10.1080/10601320701561106

URL: http://dx.doi.org/10.1080/10601320701561106

Journal of Macromolecular Science®, *Part A: Pure and Applied Chemistry* (2007) **44**, 1171–1185
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701561106

Polymer Supported Schiff Base Complexes of Iron(III), Cobalt(II) and Nickel(II) Ions and their Catalytic Activity in Oxidation of Phenol and Cyclohexene

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Received March, 2007, Accepted April, 2007

The polymer supported transition metal complexes of N,N′-bis (o-hydroxy acetophenone) hydrazine (HPHZ) Schiff base were prepared by immobilization of N,N′-bis(4-amino-o-hydroxyacetophenone)hydrazine (AHPHZ) Schiff base on chloromethylated polystyrene beads of a constant degree of crosslinking and then loading iron(III), cobalt(II) and nickel(II) ions in methanol. The complexation of polymer anchored HPHZ Schiff base with iron(III), cobalt(II) and nickel(II) ions was 83.30%, 84.20% and 87.80%, respectively, whereas with unsupported HPHZ Schiff base, the complexation of these metal ions was 80.3%, 79.90% and 85.63%. The unsupported and polymer supported metal complexes were characterized for their structures using I.R, UV and elemental analysis. The iron(III) complexes of HPHZ Schiff base were octahedral in geometry, whereas cobalt(II) and nickel(II) complexes showed square planar structures as supported by UV and magnetic measurements. The thermogravimetric analysis (TGA) of HPHZ Schiff base and its metal complexes was used to analyze the variation in thermal stability of HPHZ Schiff base on complexation with metal ions. The HPHZ Schiff base showed a weight loss of 58% at 500°C, but its iron(III), cobalt(II) and nickel(II) ions complexes have shown a weight loss of 30%, 52% and 45% at same temperature. The catalytic activity of metal complexes was tested by studying the oxidation of phenol and epoxidation of cyclohexene in presence of hydrogen peroxide as an oxidant. The supported HPHZ Schiff base complexes of iron(III) ions showed 64.0% conversion for phenol and 81.3% conversion for cyclohexene at a molar ratio of 1:1:1 of substrate to catalyst and hydrogen peroxide, but unsupported complexes of iron(III) ions showed 55.5% conversion for phenol and 66.4% conversion for cyclohexene at 1:1:1 molar ratio of substrate to catalyst and hydrogen peroxide. The product selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was 90.5% and 96.5% with supported HPHZ Schiff base complexes of iron(III) ions, but was found to be low with cobalt(II) and nickel(II) ions complexes of Schiff base. The selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was different with studied metal ions and varied with molar ratio of metal ions in the reaction mixture. The selectivity was constant on varying the molar ratio of hydrogen peroxide and substrate. The energy of activation for epoxidation of cyclohexene and phenol conversion in presence of polymer supported HPHZ Schiff base complexes of iron(III) ions was 8.9 kJ mol^{-1} and 22.8 kJ mol^{-1}, respectively, but was high with Schiff base complexes of cobalt(II) and nickel(II) ions and with unsupported Schiff base complexes.

Keywords: catalysis; metal complexes; phenol; cyclohexene; polymer and oxidation

1 Introduction

The Schiff base complexes of transition metals showed high catalytic activities in various chemical reactions such as oxidation (1, 2), epoxidation of olefins (3, 4) and polymerization of ethylene with narrow molecular weight distribution (5, 6), however, supported metal complexes have shown high catalytic activity (7, 8) and enantioselectivity (9, 10) in comparison to homogeneous catalysts. The manganese(II) salen complexes anchored on tailor made polymer support showed high enantioselectivity without any mass transfer limitation for alkenes to reach on active sites on polymer supports (11). The metal complexes used as catalysts have been immobilized on various supports (12–16), but polymer supports have shown better control on efficiency of catalysts (17, 18) due to suitable microenvironment provided by polymer chains for the substrates in comparison to zeolites (19) and silica (20) used to immobilize these catalysts. The metal complexes on solid supports are immobilized either physically (21, 22) or by forming a covalent bond between metal complexes and supports (23–25). The recovery of catalysts from physically linked catalysts was low in comparison

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to covalently bound catalysts due to leaching of catalyst. The oxidation of phenol using Schiff base complexes has been reported (26), but oxidation of phenol with polymer supported transition metal complexes has been found to be high (27) in the presence of t-butyl hydroperoxide. The polymer modified manganese ferrocyanide complex on aluminosilicates showed high catalytic activity in oxidation of cyclohexene by hydrogen peroxide for the production of cyclohexanone and cyclohexanal (28). The activity of polymer supported Schiff base complexes of metal ions in decomposition of hydrogen peroxide was influenced by the redox potential of metal ions (29), which might be a useful criterion to explain the variation in catalytic activity of various metal ions in oxidation of phenol and cyclohexene in presence of hydrogen peroxide. The transition metal complexes play a significant role in oxidation of phenol and epoxidation of olefins by reducing the activation energy of hydrogen peroxide, which is used as oxidant (30, 31). The oxidation of phenol with supported catalysts showed significant improvement due to further reduction in energy of activation of hydrogen peroxide (32). Similarly, the supported catalysts were more active in epoxidation of cyclohexene in presence of t-butyl hydroperoxide as oxidant (33, 34). The catalytic activity of polymer supported cobalt(II) complexes in decomposition of hydrogen peroxide (35, 36) showed variations with solution pH, which might be due to the change in redox potential of the catalyst. The activity of metal complexes also showed dependence on structures of Schiff base ligands used in formation of metal complexes. The oxidation of phenol and epoxidation of cyclohexene using hydrogen peroxide as an oxidant has been reported using salen complexes, but catalytic activity of metal complexes of hydrazine Schiff base is not reported in the literature, hence an attempt has been made to prepare polymer supported metal complexes of N,N′-bis(o-hydroxy acetophenone) hydrazine (HPHZ) Schiff base and to evaluate the structures of complexes and catalytic activity in oxidation of phenol and cyclohexene in the presence of hydrogen peroxide as oxidant. The activity of polymer-supported complexes has been compared with unsupported HPHZ Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions.

2 Experimental

2.1 Materials

The divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from ion exchange India Ltd. Mumbai, India for anchoring the synthesized Schiff base complexes of metal ions. The chloro salts of iron, cobalt and nickel ions were purchased from Ranbaxy, Mumbai, India and were used without further purification. The cyclohexene, phenol, hydrogen peroxide (30wt%), o-hydroxy acetophenone and hydrazine were procured from E. Merck, India. Other chemicals and solvents were of analytical grade (>99%) and used after purification by standard methods (37).

2.2 Characterization of Schiff Base and its Metal Complexes

The IR spectra of Schiff base and its metal complexes were recorded on a KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of Schiff base and its metal complexes were recorded with a Shimadzu 1601 PC UV-VIS Spectrophotometer by keeping the sample mull in a cuvette. Thermogravimetric analysis (TGA) of Schiff base and its metal complexes was carried out using a Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10°C/min. The amount of metal ions loaded on Schiff base was estimated by analyzing the loading solution with a Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_{max} of metal ions. The amount of Schiff base loaded on polymer beads and its composition was estimated using a Haraeus Carlo Ebra 1108 Elemental Analyzer. ^{1}H-NMR spectra of HPHZ Schiff base and its metal complexes were recorded on FT-NMR-Brucker-300 MHz Spectrophotometer using DMSO-d_6 as a solvent and tetramethylsilane as an internal reference. The magnetic moment (μ) of metal complexes was measured using a Vibrating Sample Magnetometer-155. The molecular weight of N,N′-bis (o-hydroxy acetophenone)hydrazine (HPHZ) Schiff base and its metal complexes was determined by a Vapor Pressure Osmometer (Knauer K-700, Germany) in dimethyl formamide as the solvent and using benzyl as the standard.

2.3 Synthesis of N,N′-bis (o-Hydroxy acetophenone) Hydrazine Schiff Base and its Metal Complexes

The N,N′-bis (o-hydroxy acetophenone) hydrazine (HPHZ) Schiff base was synthesized modifying the procedure reported in the literature (37). The reaction mixture containing o-hydroxy acetophenone (20 mmol, 2.22 g) and hydrazine (10 mmol, 0.16 g) in methanol was refluxed at 60°C for about 45 min. The reaction mixture on cooling at low temperature produced light yellow colored crystals, which were filtered and recrystallized with methanol. The metal complexes of HPHZ Schiff base were prepared taking a 100 mL methanolic solution of mixture of Schiff base (10 mmol, 2.683 g) and 10 mmol of metal ions in a round bottom flask to reflux at 70°C. After 8 h, the solution was cooled and crystalline metal complexes were obtained from the mother liquor. Finally, the metal complexes were recrystallized in methanol and dried in a vacuum desiccator.

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 N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine (AHPHZ) Schiff base was prepared by carrying out nitrosation and reduction reactions on HPHZ Schiff base and then reacting the AHPHZ Schiff base with chloromethylated polystyrene beads. The nitrosation of HPHZ Schiff base was carried out using 10 mmol (2.683 g) of HPHZ Schiff base with sodium nitrite (10 mmol) in 1 N hydrochloric acid (10 mL) at low temperature. The resulting N,N′-bis (4-nitroso-o-hydroxy acetophenone) hydrazine was filtered and washed with hot and cold water to remove reaction impurities. The reduction of N,N′-bis(4-nitroso-o-hydroxyacetophenone) hydrazine was carried out using 10 mmol of nitrosated HPHZ Schiff base in 1 N hydrochloric acid (20 mL) in the presence of metallic iron, which produced N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine (AHPHZ) Schiff base. To immobilize the prepared AHPHZ Schiff base on chloromethylated polystyrene, the methanol swollen polymer beads (5 g) were refluxed in 50 mL methanol containing 15 mmol (8.9505 g) of AHPHZ Schiff base. After 8 h, the HPHZ Schiff base anchored polymer beads were separated and dried in a vacuum desiccator. The amount of HPHZ Schiff base loaded on polymer beads was estimated with elemental analysis of HPHZ Schiff base loaded polymer beads. The HPHZ Schiff base anchored polymer beads were loaded with metal ions by keeping 5 g HPHZ Schiff base anchored polymer beads in 50 mL aqueous solution of metal ions (13 mmol) for 10 h. Finally, the polymer beads were separated and dried at 70°C in a vacuum oven after washing with hot and cold water. The loading of metal ions was determined by analyzing the loading solution with Atomic Absorption Spectrometer. The loading of metal ions on free and polymer supported HPHZ Schiff base was calculated as complexation of Schiff base using the amount of HPHZ Schiff base and metal ions loaded on polymer beads.

$$\text{Complexation of metal ions} = \frac{\text{Amount of metal ions loaded}}{\text{Amount of Schiff base used for loading}}$$

2.5 Catalytic Activity of Metal Complexes in Oxidation of Phenol and Epoxidation Cyclohexene

To evaluate the catalytic activity of free and polymer supported metal complexes of HPHZ Schiff base; the oxidation of phenol and epoxidation of cyclohexene was carried out using hydrogen peroxide as an oxidant at a fixed ionic strength (0.1 M) and hydrogen ions concentration (pH 7) in reaction mixture. To carry out these reactions, a calculated amount of metal anchored polymer beads was taken in a two-necked round-bottomed flask containing 2.0 mL acetonitrile and 0.05 M phenol (4.7 g) or 0.05 M cyclohexene (4.1 g). The oxidation of phenol and epoxidation of cyclohexene was carried out adding 5.67 g (0.05 M) hydrogen peroxide (30wt%) in the reaction mixture and 2.0 mL chlorobenzene as the internal standard. The water condenser and nitrogen inlet tube was attached with a reaction flask. The solution was stirred (1200 rpm) with a magnetic stirrer and heated to a constant temperature. To follow the reactions, the reaction mixtures were analyzed at different time intervals by a gas chromatographic method. The reactions were also studied at different molar ratios of substrates, hydrogen peroxide and catalyst in the reaction mixture. The activation energy for oxidation of phenol and epoxidation of cyclohexene was determined by studying the reactions at different temperatures at constant molar ratios of substrate to H_2O_2 and catalyst. The reactions were also studied without using catalysts to analyze the effect of an added catalyst in oxidation of phenol and epoxidation of cyclohexene. The retention times of standards were used to identify the reaction products. The product selectivity in oxidation of phenol and epoxidation of cyclohexene was determined using peak areas of chromatograms.

3 Results and Discussion

Investigations revealed that polymer supported metal complexes are sometimes more catalytic and efficient than free metal complexes and unsupported catalysts (38). The activity of catalysts also depends on the properties of polymer supports and to the amount of loaded catalysts (39, 40). The thermal stability of catalysts must be high, if used in high temperature reactions. Thermal analysis of supported metal complexes was carried out to evaluate their applications in high temperature reactions and to provide a proof for loading of metal ions on polymer anchored Schiff base ligands. Thermogravimetric analysis (TGA) of HPHZ Schiff base showed a weight loss of 58% at 500°C, but its iron(III), cobalt(II) and nickel(II) ions complexes have shown a weight loss of 30%, 52%, and 4%, respectively at the same temperature, which clearly indicated that iron(III) ions complexes were more stable in comparison to cobalt(II) and nickel(II) ions complexes. The weight loss in metal complexes at 500°C was attributed to the decomposition of HPHZ Schiff base complexes of metal ions.

Temperature of maximum rate of decomposition (T_{max}) of polymer anchored Schiff base (P-HPHZ) was increased from 221°C to 336°C on complexation with iron(III) ions and increased to 324°C and 227°C on complexation with cobalt(II) and nickel(II) ions, respectively (Figure 1). In addition to thermal analysis, the free and polymer supported metal complexes of HPHZ Schiff base were characterized by IR and UV techniques to provide a proof for complexation of metal ions as well as to predict the structures and geometry of metal complexes by considering the observed magnetic properties of the complexes.

3.1 Characterization of N,N′-bis (o-Hydroxy acetophenone) Hydrazine Schiff Base

The N,N′-bis (o-hydroxy acetophenone) hydrazine (HPHZ) Schiff base was obtained by refluxing hydrazine (HZ) and

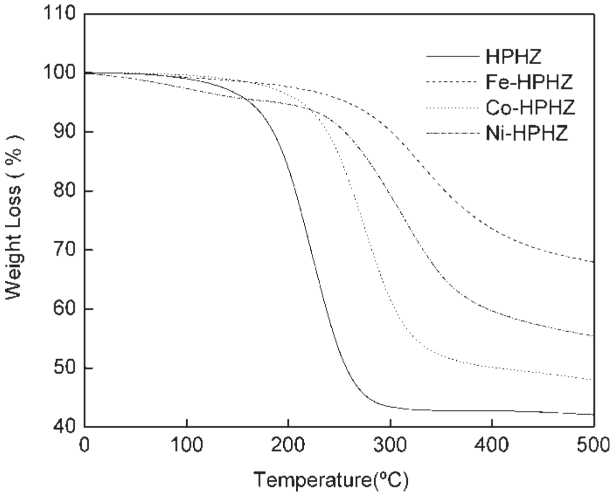


Fig. 1. Thermal stability of polymer supported HPHZ Schiff base and its metal complexes.

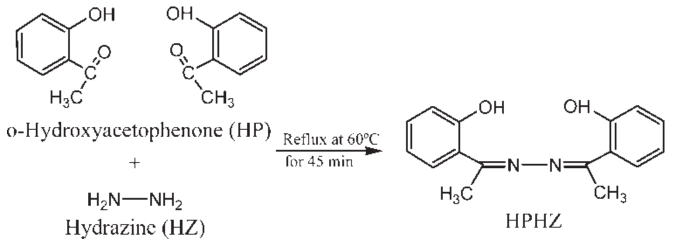
o-hydroxy acetophenone (HP) for 45 min at 60°C in methanol, which produced a substantial yield (81.79%) of HPHZ Schiff base (Scheme 1). The I.R. spectrum of HPHZ Schiff base showed absorption bands at 1621 cm^{-1} (>C=N), 1268 cm^{-1} $(>\text{C-O})_{\text{phenolic}}$ (Figure 2A) and a broad band between 3300 cm^{-1} to 2950 cm^{-1}, which was assigned to phenolic OH.

The elemental analysis of HPHZ Schiff base has shown (%): $C = 71.55$, $N = 10.27$, and $H = 5.85$, Calcd. (%): $C = 71.62$, $N = 10.44$ and $H = 6.01$, which corresponded to $C_{18}H_{20}N_2O_2$ empirical formula of HPHZ Schiff base.

The molecular weight of Schiff base was found to be 268.22 g mol^{-1} (Calcd. 268.31 g mol^{-1}). The electronic spectrum of HPHZ Schiff base (Figure 3) has shown bands at 248 nm and 317 nm, which were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The ^{1}H-NMR spectrum of HPHZ Schiff base has shown signals at $\delta/\text{ppm} = 2.15$ (3H), 5.15 (1H), 6.95 (2H), 7.25 (1H), and 7.55 (1H), which correspond to the structure of 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

The nitrosation of N,N′-bis (o-hydroxy acetophenone) hydrazine Schiff base was carried out in the presence of $NaNO_2$ and HCl, which showed 86.79% yield of N,N′-bis (4-nitroso-o-hydroxyacetophenone) hydrazine (Scheme 2). The elemental analysis of N,N′-bis (4-nitroso-o-hydroxy acetophenone) hydrazine has shown (%): $C = 58.01$, $N = 16.86$, and $H = 4.03$, Calcd. (%): $C = 58.89$, $N = 17.17$ and $H = 4.32$, which corresponds to $C_{16}H_{14}N_4O_4$ formula of nitrososated Schiff base. The molecular weight of N,N′-bis (4-nitroso-o-hydroxy acetophenone) hydrazine was found to be 298.5 g mol^{-1} (Calcd. 298.3 g mol^{-1}). The I.R. spectrum of



Sch. 1. Synthesis of N,N′-bis (o-hydroxy acetophenone) hydrazine Schiff base (HPHZ).

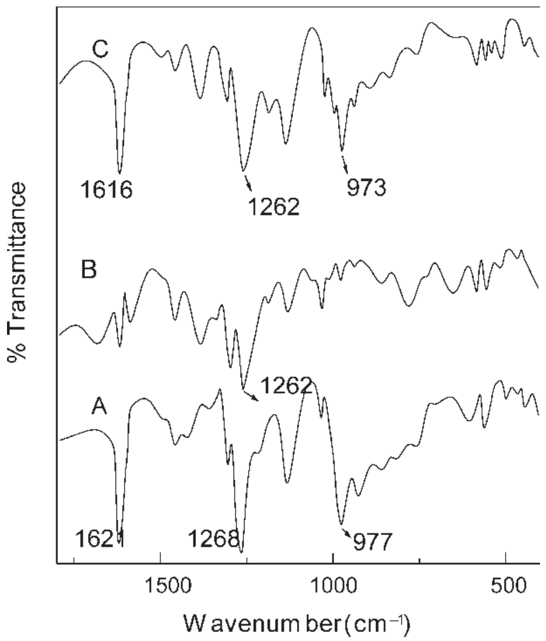


Fig. 2. FTIR spectra of free HPHZ Schiff base (A), polymer beads (B) and polymer anchored Schiff base (C).

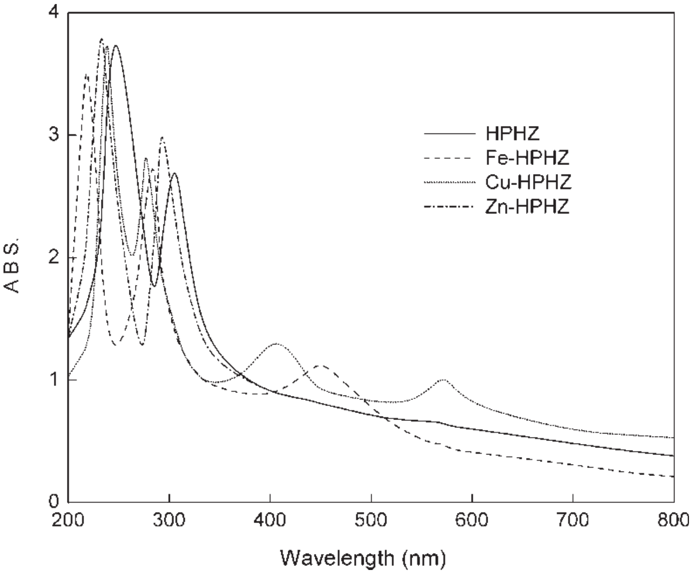
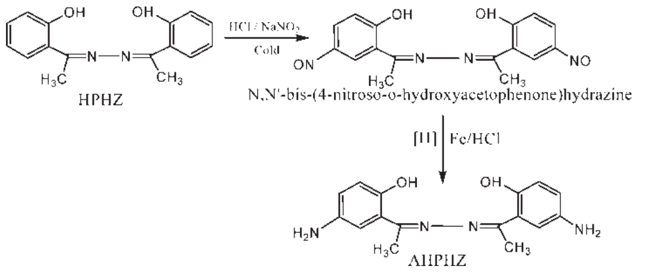
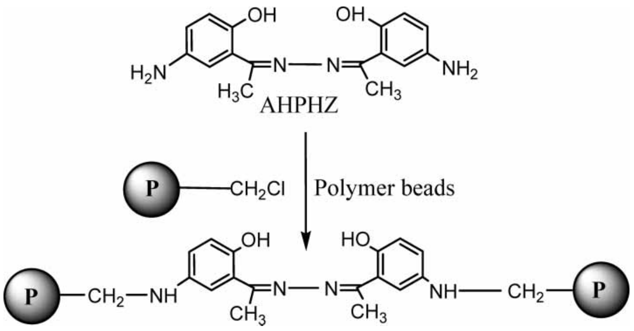


Fig. 3. Electronic spectra of HPHZ Schiff base and its metal complexes.



Sch. 2. Synthesis of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine Schiff base (AHPHZ).



Sch. 3. Synthesis of polymer anchored Schiff base (P-HPHZ).

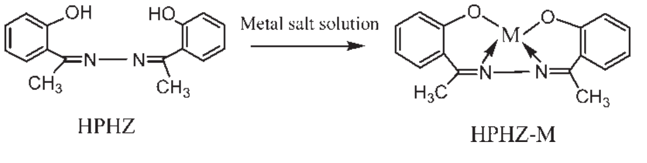
N,N′-bis (4-nitroso-o-hydroxy acetophenone) hydrazine showed absorption bands at 1630 cm^{-1} (>C═N), 1280 cm^{-1} (>C-O)$_{\text{phenolic}}$, 1550 cm^{-1} and 1335 cm^{-1} for N-O group. The nitrosation of HPHZ Schiff base showed a shift in NMR signals in comparison to NMR signals observed with a pure HPHZ Schiff base. The nitrosated HPHZ Schiff base showed proton signals at δ/ppm = 1.05 (3H), 5.15 (1H), 7.20 (1H), 7.82 (1H) and 8.15 (1H), which corresponded to the structure of nitrosated HPHZ Schiff base as shown in Scheme 2. The protons ortho to nitroso group in HPHZ Schiff base were deshielded, hence, NMR signals for these protons appeared at 7.82 ppm and at 8.15 ppm in place of 7.25 ppm and 7.55 ppm of pure HPHZ Schiff base. The proton signal at 6.95 ppm was missing due to the substitution of nitroso group in the benzene. The N,N′-bis (4-nitroso-o-hydroxy acetophenone) hydrazine was reduced with iron(III) ions in the presence of hydrochloric acid, which gave an 85.82% yield of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine Schiff base (AHPHZ) as shown in Scheme 2. The AHPHZ was characterized for its m.p., which was 189°C. The elemental analysis of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine Schiff base showed (%): C = 63.32, N = 18.0 and H = 5.58, Calcd. (%): C = 64.41, N = 18.78, and H = 6.08, which corresponded to the $C_{16}H_{18}N_4O_2$ empirical formula of Schiff base. The molecular weight of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine was found to be 299.1 g mol^{-1} (Calcd. 298.3 g mol^{-1}).

The I.R. spectrum of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine has shown absorption bands at 1621 cm^{-1} (>C═N), 1268 cm^{-1} (>C-O)$_{\text{phenolic}}$ and a band between 1633–1650 cm^{-1} (>C-N). The NMR spectrum of AHPHZ showed proton signals at δ/ppm = 2.15 (3H), 4.15 (2H), 5.15 (1H), 6.45 (1H), 6.65 (1H), 6.85 (1H), which correspond to the structure of AHPHZ Schiff base as shown in Scheme 2. The synthesized N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine Schiff base (AHPHZ) was anchored on divinyl benzene cross-linked chloromethylated polystyrene beads by refluxing AHPHZ Schiff base with polymer beads in DMF for 8 h at 60°C. The amount of AHPHZ Schiff base anchored on polymer beads was found to be 85%, which corresponded to 2.55 mmol of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine Schiff base on 1 g of polymer beads (Scheme 3). The anchoring of N,N′-bis (4-amino-o-hydroxy acetophenone) hydrazine on polymer beads was confirmed by analyzing the I.R. spectrum of HPHZ anchored polymer beads (Figure 2C) with I.R. spectrum (Figure 2B) of pure polymer beads.

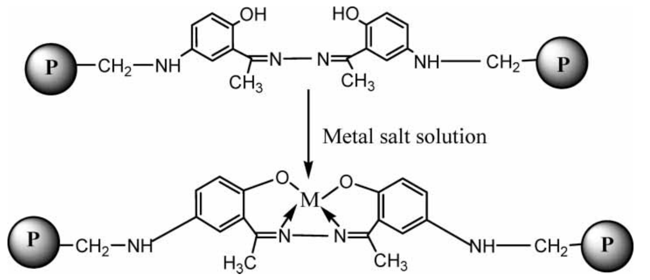
The I.R. spectrum of polymer anchored Schiff base (Figure 2C) showed new absorption bands at 1616 cm^{-1} (>C═N), 1260 cm^{-1} (>C-O)$_{\text{phenolic}}$ and a broad band between 2955–3373 cm^{-1} (>C-N), which were absent in the I.R. spectrum of pure polymer beads (Figure 2B), but was present in spectrum of free Schiff base (Figure 2A). The I.R. spectrum of pure polymer beads has shown an absorption band at 1262 cm^{-1} (Figure 2B), which has been attributed to C-Cl bond of chloromethyl present in cross-linked polymer beads. The low intensity for absorption band at 1262 cm^{-1} in HPHZ Schiff base anchored polymer beads (Figure 2C) in comparison to pure polymer beads (Figure 2B), was a concrete proof for anchoring of HPHZ Schiff base on polymer beads. The appearance of new absorption bands and shift in characteristic absorption bands of HPHZ Schiff base was also considered as evidence for anchoring the 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

The loading of metal ions on free and polymer supported HPHZ Schiff base was carried out by refluxing free Schiff base (Scheme 4) and polymer anchored Schiff base in a solution of metal salt at 60°C for 6 h (Scheme 5). The metal complexes of free Schiff base (HPHZ-M) and polymer anchored Schiff base (P-HPHZ-M), after separation and



Sch. 4. Loading of metal ions on unsupported Schiff base (HPHZ-M).



Sch. 5. Loading of metal ions on polymer supported Schiff base (P-HPHZ-M).

purification, were characterized to ascertain their structures and loading of metal ions. The complexation of iron(III) ions on free Schiff base and polymer anchored Schiff base was 80.30% and 83.20%, respectively (Table 1), whereas complexation of cobalt(II) ions on free and polymer supported Schiff base was 79.90% and 84.30%. The complexation of nickel(II) ions was 85.63% on free Schiff base and 87.80% on polymer supported Schiff base, which was highest in that shown by iron(III) and cobalt(II) ions.

The results as shown in Table 1 have clearly suggested that the metal ions loading on polymer supported HPHZ Schiff base was higher than free HPHZ Schiff base. The complexation of metal ions with HPHZ Schiff base showed significant variations in I.R. bands for >C=N and >C-O groups and new absorptions bands appeared, due to the formation of M-O and M-N bonds in metal complexes (Figure 4). The disappearance of a phenolic absorption band at 1260 cm^{-1} of HPHZ Schiff base (Figure 4A) after metal ions complexation (Figures 4B, C and D) has provided evidence for complexation of metal ions with HPHZ Schiff base. The polymer supported Schiff base showed absorption bands at low frequency (Figure 4A) in comparison to free Schiff base (Figure 2A). On complexation with iron(III) ions, the frequency of >C=N absorption band of free Schiff base has decreased from 1621 cm^{-1} to 1595 cm^{-1}, whereas polymer supported Schiff base showed a variation from 1616 cm^{-1} to 1591 cm^{-1} (Figures 4A and B).

Table 1. Complexation of metal ions (wt%) on free (HPHZ) and polymer supported Schiff base (P-HPHZ)

Schiff base	Iron(III) ions	Cobalt(II) ions	Nickel(II) ions
HPHZ	80.30	79.90	85.63
P-HPHZ	83.20	84.30	87.80

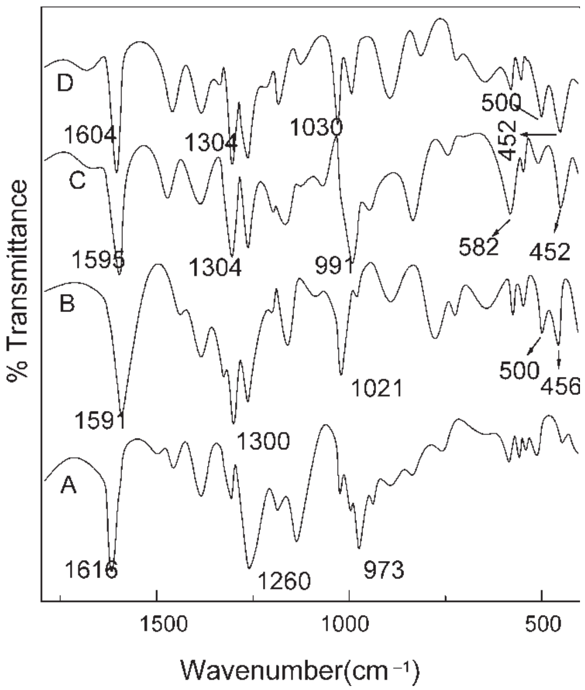
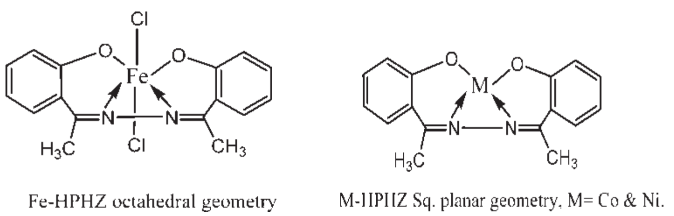


Fig. 4. FT-IR spectra of polymer supported HPHZ Schiff base (A) and its metal complexes (B, C, D).

The complexation of cobalt(II) and nickel (II) ions with polymer supported Schiff base showed absorption bands at 1595 cm^{-1} and 1604 cm^{-1} (Figures 4C and D) in place of 1616 cm^{-1} (Figure 4A). These variations in I.R. bands corresponding to >C=N group of Schiff base was considered as an evidence for metal ions interactions with azomethyne nitrogen (>C=N) of HPHZ Schiff base. The complexation of iron(III) ions showed new absorption band at 465 cm^{-1} with free Schiff base, and at 456 cm^{-1} with polymer anchored Schiff base, which was due to the formation of M-N bond between iron(III) ions and Schiff base (Figure 4B). The complexation of cobalt(II) ions showed absorption bands at 456 cm^{-1} and 452 cm^{-1} for M-N bond with free and polymer supported Schiff base (Figure 4C), whereas complexation of nickel(II) ions with free and polymer supported Schiff base showed absorption bands at 456 cm^{-1} and 452 cm^{-1} (Figure 4D) for M-N bond formation. The complexation of iron(III), cobalt(II) and nickel(II) ions has also shown another new band due to the formation of bond between metal ions and phenolic oxygen (-O-M).

The complexation of iron(III), cobalt(II) and nickel(II) ions with polymer supported Schiff base has produced M-O absorption band at 500 cm^{-1}, 582 cm^{-1} and 500 cm^{-1}, respectively (Figures 4B, C and D). The complexation of metal ions with Schiff base was further confirmed by comparing the electronic spectra of metal complexes and pure HPHZ Schiff base (Figure 2). The complexation of iron(III) ions with HPHZ Schiff base has shown a variation in $\pi \rightarrow \pi^*$ transition from 248 nm to 219 nm, but in the case of cobalt(II) and nickel(II) ions, the $\pi \rightarrow \pi^*$ transition appeared at 226 nm and 241 nm. The $n \rightarrow \pi^*$ transition of HPHZ Schiff base was shifted from 317 nm to 285 nm on complexation with iron(III) ions, whereas in case of cobalt(II) and nickel(II) ions, the $n \rightarrow \pi^*$ transition was observed at 271 nm and 263 nm. The CT and $d \rightarrow d$ transitions also provided evidences for complexation of metal ions with Schiff base. The complexation of cobalt(II) and



Sch. 6. Geometry and structures of Schiff base complexes of metal ions.

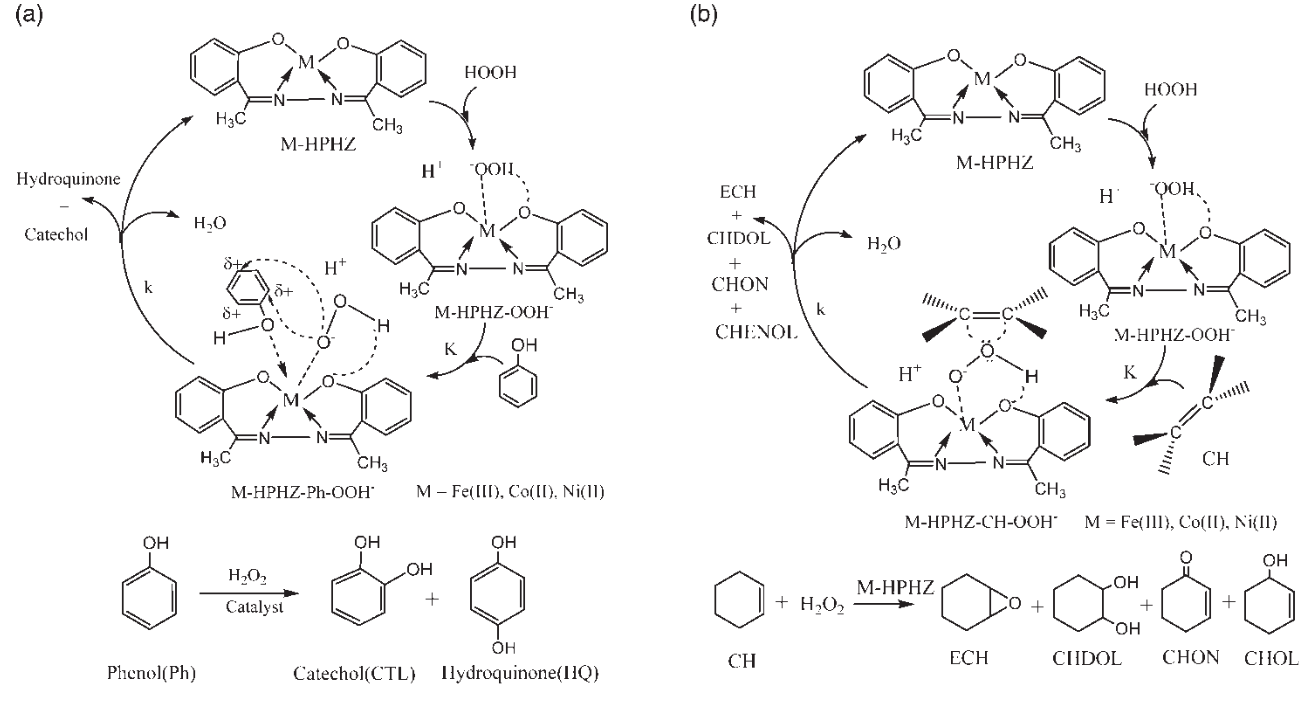
nickel (II) ions with HPHZ Schiff base has shown a CT transition at 378 nm and 313 nm, but no CT transition was shown by iron(III) complexes. The complexation of iron(III), cobalt(II) and nickel(II) ions with HPHZ Schiff base showed d → d transitions at 449 nm, 438 nm and 402 nm, respectively, which corresponded to $t_{2g}^5\ e_g^0$, $t_{2g}^6\ e_g^1$ and $t_{2g}^6\ e_g^2$ electronic configurations for iron(III), cobalt(II) and nickel(II) ions in these complexes. The magnetic moment (μ) of Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions was found to be 1.73 BM, 1.73 BM and 0.0 BM, respectively, which indicated that iron(III) and cobalt(II) ions complexes were paramagnetic in nature with one unpaired electron in each and nickel(II) ions complexes were diamagnetic in nature with all paired electrons. The magnetic moment (μ) and electronic configurations of metal complexes suggested octahedral geometry with d^2sp^3 hybridization for iron(III) complexes and dsp^2 hybridization with square planar geometry for cobalt(II) and nickel(II) ions complexes (Scheme 6).

3.4 Oxidation of Phenol and Epoxidation of Cyclohexene

The catalytic activity of free and polymer supported metal complexes of HPHZ Schiff base was evaluated by studying the oxidation of phenol and epoxidation of cyclohexene in the presence of hydrogen peroxide. Gas chromatography was used for product selectivity and to estimate percent conversion of phenol and cyclohexene. The catechol was a major reaction product in oxidation of phenol (Scheme 7a), whereas epoxy cyclohexane (ECH) was in epoxidation of cyclohexene (Scheme 7b). The formation of reaction products was attributed to enzymatic behavior of metal complexes of HPHZ Schiff base. The free and polymer supported Schiff base complexes of metal ions (HPHZ-M) produced active species (M-HPHZ-HOO$^-$) through fast interactions with hydrogen peroxide and HPHZ Schiff base.

The active species has produced intermediates (M-HPHZ-Ph-OOH$^-$) and (M-HPHZ-CH-HOO$^-$) through interactions of phenol and cyclohexene in a rapid equilibrium (K). The intermediate (M-HPHZ-Ph-OOH$^-$) has facilitated the nuceophilic attack of OOH$^-$ species on ortho and para position on phenol to produce hydroxy substituted phenols (Scheme-7a), whereas the intermediate (M-HPHZ-CH-OOH$^-$) has assisted in transfer of oxygen to produce epoxy cyclohexane (ECH) and other reaction products (CHOL, CHDOL and CHON) through a slow reaction step (k) (Scheme 7b) in the epoxidation of cyclohexene.

The polymer support has facilitated the decomposition of intermediates; hence, percent conversion of phenol and cyclohexene was higher with polymer supported metal complexes (Figures 5 and 6) in comparison to free metal complexes of



Sch. 7. (a) Oxidation of phenol. (b) Epoxidation of cyclohexene.

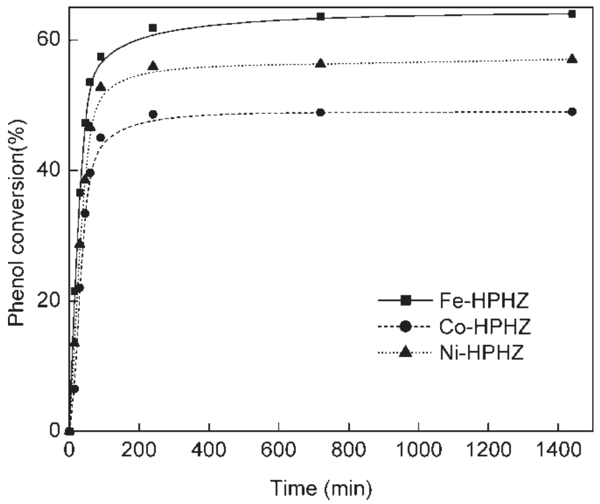


Fig. 5. Effect of reaction time on oxidation of phenol in presence of polymer supported metal complexes. [Phenol]:[Catalyst]:[H_2O_2] = 1:1:1 (0.05 M), Temp. = 70°C.

HPHZ Schiff base (Table 2). The conversion of phenol and cyclohexene was initially high up to 240 min, and then after the conversion became almost constant due to the substantial decrease in concentration of oxidant and substrate in the reaction mixture (Figures 5 and 6). Similar trends in substrate conversion were observed with unsupported catalysts at different time intervals as found with unsupported catalysts (Figures 5 and 6). The oxidation and epoxidation reactions also showed dependence on type of catalyst as is clear from substrate conversion in presence of HPHZ Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions (Table 2, Figures 5 and 6). The percent conversion of phenol and cyclohexene was more with Schiff base complexes of iron(III) in comparison to cobalt(II) and nickel(II) ions.

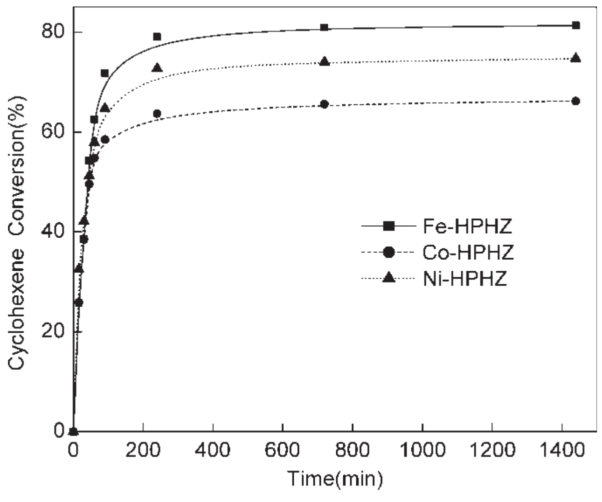


Fig. 6. Effect of reaction time on epoxidation of cyclohexene in the presence of polymer supported metal complexes. [Cyclohexene]:[Catalyst]:[H_2O_2] = 1:1:1 (0.05 M), Temp. = 40°C.

Table 2. Catalytic activity of unsupported metal complexes (M-HPHZ) in oxidation of phenol (Ph) and epoxidation of cyclohexene (CH)

	Percent conversion (%)					
	Fe-HPHZ		Co-HPHZ		Ni-HPHZ	
Time/min	Ph	CH	Ph	CH	Ph	CH
0	0	0	0	0	0	0
15	7.9	14.9	3	16.2	3.3	10.8
30	17.5	26.0	9.2	24.2	9.1	20.3
45	27.2	36.4	17.4	31.9	17.9	29.9
60	34.4	43.7	22.4	37.2	23.7	35.2
90	40.7	53.4	27.1	42.9	31.6	47.0
240	48.0	63.6	34.3	50.2	38.1	61.6
720	50.0	65.2	35.7	52.2	39.1	63.9
1440	50.5	66.4	36.4	52.5	39.8	64.2

[H_2O_2]:[Catalyst]:[Phenol]/[Cyclohexene] = 1:1:1 (0.05 M), Temp. = 70°C (Ph), 40°C (CH).

The high activity of catalyst on polymer support was more due to the suitable interactions of catalyst with substrate than is possible with unsupported catalysts. The low activity of catalyst in solution was due to the formation of inactive dimers or multimers of metal complexes in the solution. The amount of phenol oxidized with hydrogen peroxide was almost equal to the final amount of catechol and phenol, which discarded the formation of other reaction products such as polymeric phenols.

The reaction products in oxidation of phenol corresponded to catechol (CTL) and hydroquinone (HQ), but the catalyst showed high selectivity for catechol (Scheme 7a). The oxidation of cyclohexene by hydrogen peroxide produced 1,2-cyclohexanediol (CHDOL), 2-cyclohexene-1-one (CHON), 2-cyclohexene-1-ol (CHOL) as minor products and epoxy cyclohexane (ECH) as a major product (Scheme 7b). The catalysts used in epoxidation and oxidation reactions were recycled and reused to evaluate their catalytic activity after their applications in oxidation of phenol and in epoxidation of cyclohexene. The efficiency of supported catalysts in conversion of phenol and cyclohexene was found to be almost constant up to six recycles, and then after, the efficiency of catalysts was decreased (Table 3).

The fresh and recycled catalysts showed higher efficiency in epoxidation of cyclohexene than in oxidation of phenol (Table 3), but product selectivity for catechol and epoxy cyclohexane remained unaffected in recycled catalyst, which was an indication that the structure of metal complexes on polymer support remained unaffected after recycling as verified by comparing the I.R. spectra of recycled and freshly prepared catalysts. The activity of metal complexes in substrate conversion was evaluated under different experimental conditions for using catalysts efficiently in substrate conversion and product selectivity. The activity of HPHZ Schiff base complexes on percent conversion and product selectivity was

Table 3. Efficiency of recycled supported catalysts (P-HPHZ-M) in oxidation of phenol and epoxidation of cyclohexene

Cycle no	P-HPHZ-Fe	P-HPHZ-Co	P-HPHZ-Ni
Conversion of phenol (%)			
0	64.0	49.0	57.0
2	64.0	49.0	57.0
4	64.0	48.8	56.9
6	63.8	48.8	56.7
8	55.0	42.4	49.2
10	48.3	35.0	42.6
Conversion of cyclohexene (%)			
0	81.3	66.2	74.7
2	81.3	66.2	74.7
4	81.1	66.0	74.1
6	81.0	65.5	73.9
8	75.8	58.7	61.6
10	60.2	43.5	51.8

$[H_2O_2]$:[Catalyst]:[Phenol]/[Cyclohexene] = 1:1:1 (0.05 M), Time = 1440 min., Temp. = 70°C (Ph), 40°C (CH), CH_3CN = 2.0 mL.

studied at different molar ratio of substrate to hydrogen peroxide and catalysts and at different reaction temperatures to evaluate the energy of activation for oxidation and epoxidation reactions at constant molarity of reactants.

3.4.1 *Effect of H_2O_2 Concentration on Oxidation of Phenol and Epoxidation of Cyclohexene*

The oxidation of phenol and epoxidation of cyclohexene was studied by varying the molar ratio of H_2O_2 to phenol from 0.5–2.0 at constant molarity of substrate and catalyst (0.05 M) in acetonitrile (2.0 mL). The reaction temperature was maintained as 40°C and 70°C during epoxidation of cyclohexene and oxidation of phenol. On varying the molar ratio of hydrogen peroxide from 0.5 to 1.0 with molar ratio of phenol/cyclohexene and catalysts, the conversion of phenol and cyclohexene in presence of HPHZ Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions was increased (Figures 7 and 8), but on further increasing the molar ratio of H_2O_2 (>1) in the reaction mixture, the conversion of phenol and cyclohexene showed a decreasing trend. Similar trend was observed with unsupported HPHZ Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions. The decreasing trend in phenol and cyclohexene conversion at high molar ratio of hydrogen peroxide (>1) was attributed to the decrease in molar ratio of phenol/cyclohexene and catalyst with respect to the molar ratio of H_2O_2. The conversion of phenol (Figure 7) and cyclohexene (Figure 8) was high with HPHZ Schiff base complexes of iron(III) and low with cobalt(II) ions complexes as found during variation in molar ratio of hydrogen peroxide.

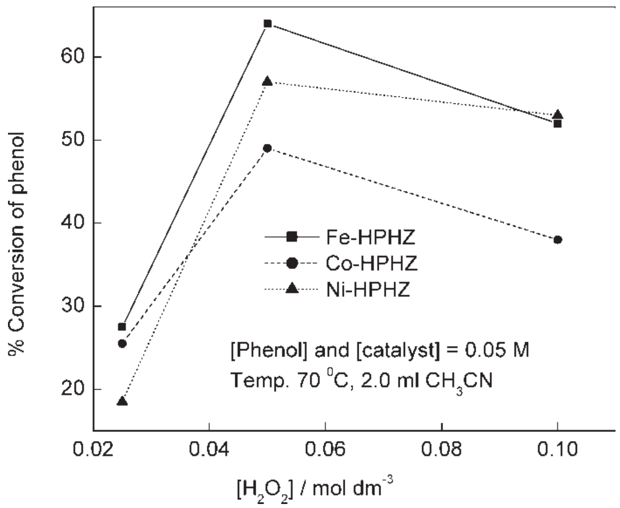


Fig. 7. Effect of H_2O_2 concentration on phenol conversion. [Phenol]:[Catalyst] = 1:1 (0.05 M), Temp. = 70°C.

During molar ratio variations of hydrogen peroxide, the selectivity for catechol (CTL) in oxidation of phenol and epoxy cyclohexane (ECH) in epoxidation of cyclohexane was almost constant in presence of Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions (Table 4). During molar ratio variations of hydrogen peroxide, the average selectivity for catechol was around 90% and was around 96% for epoxy cyclohexane (ECH) in presence of Schiff base complexes of iron(III) ions, which was significantly high in comparison to epoxidation reported at equimolar ratio of oxidant and cyclohexene (41, 42). The selectivity for catechol in presence of metal complexes was high in comparison to selectivity for catechol reported in the literature (32). The average selectivity for catechol (88%) and epoxy cyclohexane (94%) was lowest in presence of HPHZ Schiff base complexes of cobalt(II) ions.

The selectivity for epoxy cyclohexane was high with all metal complexes of HPHZ Schiff base in comparison to selectivity for catechol, which clearly indicated that HPHZ Schiff base complexes were more efficient to catalyze the

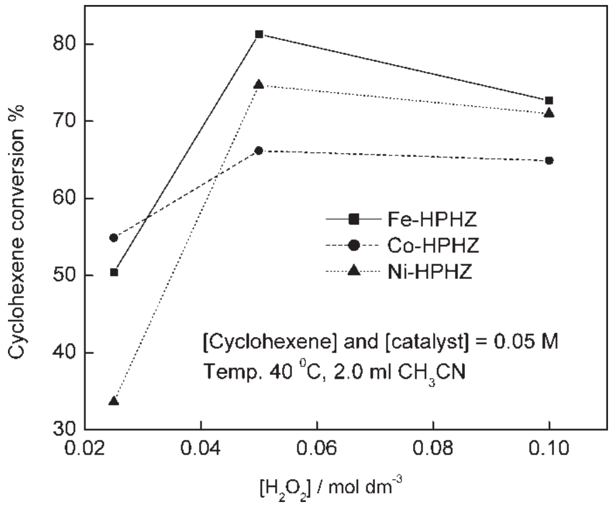


Fig. 8. Effect of H_2O_2 concentration on cyclohexene conversion. [Phenol]:[Catalyst] = 1:1(0.05 M), Temp. = 40°C.

Table 4. Effect of concentration of phenol, cyclohexene and hydrogen peroxide on product selectivity

Molarity	P-HPHZ-Fe	P-HPHZ-Co	P-HPHZ-Ni
Selectivity for catechol (CTL) in oxidation of phenol (%)			
$[H_2O_2]$			
0.025	90.4	88.8	90.1
0.05	90.5	88.9	90.3
0.1	90.5	88.9	90.4
[Phenol]			
0.025	90.3	88.8	90.2
0.05	90.5	88.9	90.3
0.1	90.5	88.9	90.3
Selectivity for epoxy cyclohexane (ECH) in oxidation of cyclohexene(%)			
$[H_2O_2]$			
0.025	96.4	94.1	95.8
0.05	96.5	94.2	95.8
0.1	96.5	94.2	95.9
[CH]			
0.025	96.4	94.1	95.8
0.05	96.5	94.2	95.9
0.1	96.5	94.2	95.8

[Catalyst] = 0.05 M, Temp. = 70°C (Ph), 40°C (CH), Time =1440 min, CH_3CN = 2.0 mL.

epoxidation of cyclohexene in comparison to oxidation of phenol. The rate of phenol conversion was high (2.13×10^{-6} $ML^{-1}\,s^{-1}$) in presence of Schiff base complex of iron(III) ions in comparison to Schiff base complexes of cobalt(II) ions and nickel(II) ions in which the rate of phenol conversion was $1.70 \times 10^{-6}\,ML^{-1}\,s^{-1}$ and $1.98 \times 10^{-6}\,ML^{-1}\,s^{-1}$, respectively (Table 5). The rate of phenol conversion and selectivity for catechol was found to be low with unsupported Schiff base complexes of metal ions.

In epoxidation of cyclohexane, the rate of cyclohexene conversion (Rp) was high ($2.74 \times 10^{-6}\,ML^{-1}\,s^{-1}$) with Schiff base complexes of iron(III) ions and low ($2.30 \times 10^{-6}\,ML^{-1}s^{-1}$) with Schiff base complexes of cobalt(II) ions (Table 6). The turnover number (TON) for oxidation of phenol was high ($14.38\,g\,mol^{-1}$ Fe hr^{-1}) in presence of iron(III) complexes in comparison to Schiff base complexes of cobalt(II) ($11.52\,g\,mol^{-1}$ Co hr^{-1}) and nickel(II) ions ($13.40\,g\,mol^{-1}$ Ni hr^{-1}) at optimum molar ratio (1:1:1) of H_2O_2 to phenol and catalyst (Table 5).

The turnover number for free and supported Schiff base complexes of metal ions in epoxidation of cyclohexene was high (Table 6) in comparison to turnover number shown by Schiff base complexes of metal ions in oxidation of phenol (Table 5). The rate of substrate conversion and turnover number, both in oxidation of phenol and in epoxidation of cyclohexene showed significant variation on varying the molar ratio of hydrogen peroxide (Tables 5 and 6), but product selectivity in both cases was almost constant (Table 4).

3.4.2 *Effect of Substrate Concentration on Oxidation and Epoxidation*

The catalytic efficiency of metal complexes in oxidation of phenol and epoxidation of cyclohexene was evaluated at different molar ratios of phenol and cyclohexene to molar ratio of hydrogen peroxide and catalyst. The molar ratio of phenol and cyclohexene was varied from 0.5 to 2.0 with respect to molar ratio of hydrogen peroxide and catalyst. During molar ratio variation of phenol and cyclohexene, the molarity of hydrogen peroxide and catalyst was constant (0.05 M). On increasing the molar ratio of phenol and cyclohexene from 0.5 to 1.0 in the reaction mixture, the conversion of phenol and cyclohexene increased substantially in presence of polymer supported metal complexes of HPHZ Schiff base (Figures 9 and 10) but on further increasing the molar ratio of phenol and cyclohexene (>1), the conversion of phenol and cyclohexene decreased (Figures 9 and 10). The decreasing trends in substrate conversion at high molar ratio of phenol and cyclohexene (>1) was due to the significant decrease in molar ratio of hydrogen peroxide and catalysts in the reaction mixture in comparison to molar ratio of substrates; hence, the conversion of phenol and cyclohexene was decreased. But the conversion of phenol and cyclohexene was optimum at 1:1:1 molar ratio of phenol/cyclohexene to hydrogen peroxide and catalysts. The product selectivity for catechol (CTL) and epoxy cyclohexane (ECH) during molar ratio variation of phenol

Table 5. Phenol conversion, selectivity for catechol (CTL) and kinetic parameter at optimum molar ratio of phenol to hydrogen peroxide and catalyst

Catalysts	Conversion (%)	Selectivity (%)	Rp × 10^6/ $ML^{-1}s^{-1}$	TON/g mol $(M)^{-1}hr^{-1}$	Ea/kJ mol^{-1}
With unsupported catalysts (HPHZ-M)					
HPHZ-Fe	56.0	86.0	1.94	13.13	23.1
HPHZ-Co	42.0	76.0	1.46	9.87	56.8
HPHZ-Ni	50.0	80.0	1.74	11.75	54.0
With supported catalysts (P-HPHZ-M)					
P-HPHZ-Fe	64.0	90.5	2.13	14.38	22.8
P-HPHZ-Co	49.0	88.9	1.70	11.52	50.95
P-HPHZ-Ni	57.0	90.3	1.98	13.40	49.18

$[H_2O_2]$:[Catalyst]:[Phenol] = 1:1:1 (0.05 M), Time = 1440, min, Temp. =70°C, CH_3CN = 2.0 mL.

Table 6. Cyclohexene (CH) conversion, selectivity of epoxy cyclohexane (ECH) and kinetic parameters at optimum molar ratio of CH to H_2O_2 and catalyst

Catalysts	Conversion (%)	Selectivity (%)	Rp × 10^6/ $ML^{-1}s^{-1}$	TON/g mol $(M)^{-1}hr^{-1}$	Ea/kJ mol^{-1}
With unsupported catalysts (HPHZ-M)					
HPHZ-Fe	72.0	92.0	2.50	14.76	11.6
HPHZ-Co	56.0	88.0	1.94	11.47	26.2
HPHZ-Ni	68.0	92.0	2.36	13.94	24.3
With supported catalysts (P-HPHZ-M)					
P-HPHZ-Fe	79.0	96.5	2.74	16.20	8.9
P-HPHZ-Co	66.2	94.2	2.30	13.51	20.0
P-HPHZ-Ni	74.7.0	95.9	2.59	15.32	18.2

$[H_2O_2]$:[Catalyst]:[Cyclohexene] = 1:1:1 (0.05 M), Time = 1440 min., Temp. = 40°C, CH_3CN = 2.0 mL.

and cyclohexene was constant (Table 4). The selectivity for catechol during molar ratio variation in phenol was around 90% with Schiff base complexes of iron(III) ions and was around 88% with Schiff base complexes of cobalt(II) ions (Table 4). A similar trend in selectivity for epoxy cyclohexane was observed with Schiff base complexes of iron(III) and cobalt(II) ions, which indicated that the electron transfer mechanism in intermediates(M-HPHZ-Ph-OOH^-) and (M-HPHZ-CH-OOH^-) in Schemes 7a and b remained unaffected on varying the molar ratio of phenol and cyclohexene in the reaction mixture as it remained unaffected during molar ratio variation of hydrogen peroxide in oxidation of phenol and epoxidation of cyclohexene. Therefore, the selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was constant during molar ratio variation of hydrogen peroxide and substrates (Table 4).

The higher conversion and selectivity in cyclohexene than phenol was due to the low energy of activation for intramolecular electron transfer reaction during decomposition of intermediate in epoxidation of cyclohexene (Scheme 7b) than the activation energy for intermolecular electron transfer reaction in the intermediate of phenol oxidation (Scheme 7a). The rate (Rp) of phenol conversion and epoxidation of cyclohexene increased more on increasing the molar ratio of substrate (phenol/cyclohexene) form 0.5 to 1.0 than the increase in rate (Rp) of phenol conversion and epoxidation of cyclohexene on increasing the molar ratio of hydrogen peroxide and catalysts from 0.5 to 1.0 in the reaction mixture. The rate of phenol oxidation was high (2.13×10^{-6} ML^{-1} s^{-1}) at a 1:1:1 molar ratio of phenol to H_2O_2 and Schiff base complex of iron(III) ions (Table 5). The rate of epoxidation of cyclohexene was also high (2.74×10^{-6} $ML^{-1}s^{-1}$) at a 1:1:1 molar ratio of cyclohexene to H_2O_2 and Schiff base complex of iron(III) ions (Table 6).

The rate of oxidation of phenol and epoxidation of cyclohexene in both reactions was low with Schiff base complexes cobalt(II) ions at a 1:1:1 molar ratio of substrate to H_2O_2 and catalyst (Tables 5 and 6). The turnover number increased with the increase in molar ratio of phenol/cyclohexene in the reaction mixture and was high at a molar ratio of 1:1:1 of

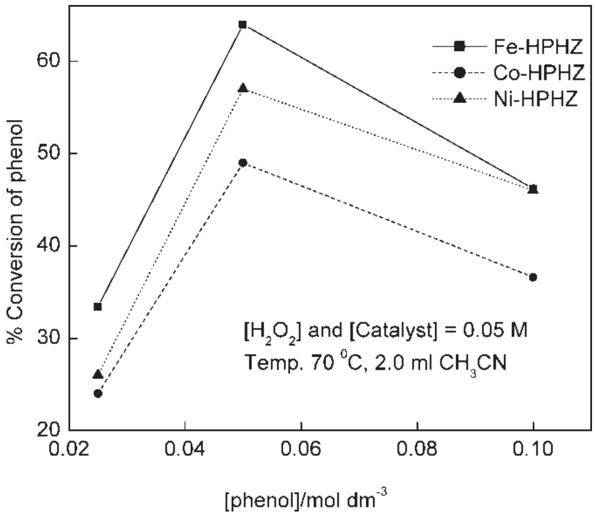


Fig. 9. Effect of phenol concentration on its oxidation. $[H_2O_2]$:[Catalyst] = 1:1(0.05 M), Temp. = 70°C.

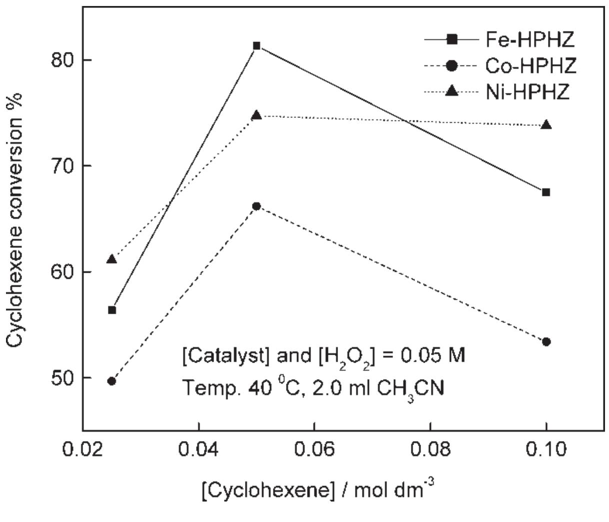


Fig. 10. Effect of cyclohexene concentration on its oxidation. $[H_2O_2]$:[Catalyst] = 1:1 (0.05 M), Temp. = 40°C.

phenol/cyclohexene to hydrogen peroxide and catalyst (Tables 5 and 6). The Schiff base complexes of iron(III) showed high turnover number in both reactions. The turnover number of supported catalyst was higher than free catalyst.

3.4.3 *Effect of Catalyst Concentration in Oxidation and Epoxidation*

The activity of polymer supported metal complexes in oxidation of phenol and epoxidation of cyclohexene was evaluated using different molar ratios of catalysts to oxidant and substrates.

The molar ratio of Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions varied from 0.5 to 2.0 at constant molarity (0.05 M) of substrate (phenol/cyclohexene) and hydrogen peroxide in the reaction mixture. The conversion of phenol and cyclohexene increased on increasing the molar ratio of catalysts from 0.5 to 1.0 and 64% conversion of phenol and 81.3% conversion of cyclohexene was observed with Schiff base complexes of iron(III) at a molar ratio of 1:1:1 of catalyst to hydrogen peroxide and phenol/cyclohexene (Figures 11 and 12).

The activity of complexes of cobalt(II) and nickel(II) ions was maximum at a 1:1:1 molar ratio of catalysts in conversion of phenol and cyclohexene (Figures 11 and 12). The further increase in molar ratio of complexes of metal ions (>1) in the reaction mixture, the conversion of phenol and cyclohexene was decreased (Figures 11 and 12). The decreasing trend in conversion of phenol and cyclohexene at high molar ratio of catalyst was attributed to the decrease in molar ratio of phenol/cyclohexene (<1) to the molar ratio of catalyst, which resulted in a substantial decrease in concentration of intermediates (Schemes 7a and b) in the reaction mixture to form the reaction products through its decomposition in a fast equilibrium step. The decreasing trend in conversion of phenol and cyclohexene at low molar ratio of catalyst (0.5) to phenol/cyclohexene and hydrogen peroxide was due to an insufficient amount of catalysts in the reaction mixture in comparison to phenol/cyclohexene and hydrogen peroxide (Figures 11 and 12), which decreased the formation of active species in the reaction mixture and subsequent decrease in concentration of reaction intermediates to form the reaction products (Schemes 7a and b). The variation in molarity of catalyst showed a significant effect on selectivity for catechol (CTL) in oxidation of phenol and epoxy cyclohexane (ECH) in epoxidation of cyclohexene (Table 7). The selectivity for catechol (CTL) was increased from 87.2% to 90.5%, and for epoxy cyclohexane (ECH), the selectivity was increased from 92.8% to 96.5% on increasing the molar ratio of HPHZ Schiff base complexes of

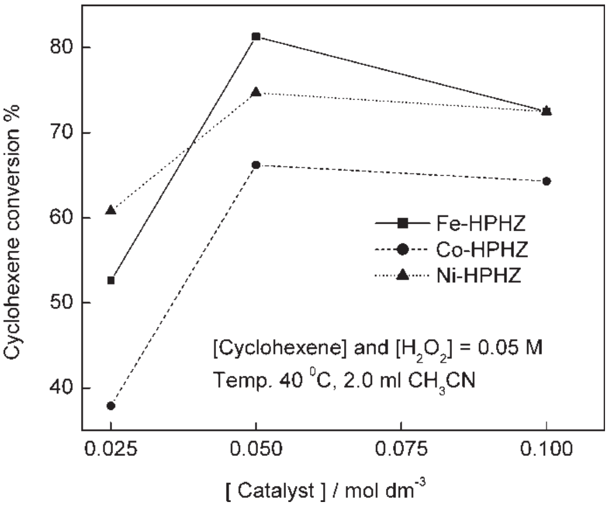


Fig. 12. Effect of supported catalyst concentration on epoxidation of cyclohexene. [Phenol]:[H_2O_2] = 1:1(0.05 M), Temp. = 40°C.

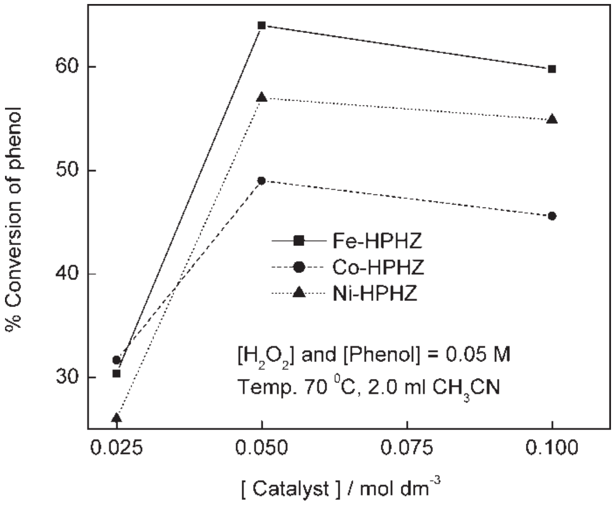


Fig. 11. Effect of supported catalyst concentration on oxidation of phenol. [Phenol]:[H_2O_2] = 1:1(0.05 M), Temp. = 70°C.

Table 7. Effect of supported catalyst concentration on selectivity for catechol (CTL) and epoxy cyclohexane (ECH)

Molarity of catalyst/M	Selectivity for catechol (%)	Selectivity for epoxy cyclohexane (%)
P-HPHZ-Fe		
0.025	87.2	92.8
0.05	90.5	96.5
0.100	89.2	95.1
P-HPHZ-Co		
0.025	85.7	90.1
0.05	88.9	94.2
0.1	86.0	93.4
P-HPHZ-Ni		
0.025	86.4	91.8
0.05	90.3	95.9
0.100	89.1	95.0

[H_2O_2]:[Phenol]:[Cyclohexene] = 1:1:1 (0.05 M), Time = 1440 min., Temp. = 70°C (Ph), 40°C (CH), CH_3CN = 2.0 mL.

iron(III) ions in the reaction mixture (Table 7) and on further increasing the molar ratio of iron(III) complexes (>1), the selectivity for catechol (CTL) and epoxy cyclohexane (ECH) decreased to 89.2% and 95.1%, respectively. The trend in selectivity for catechol (CTL) and epoxy cyclohexane (ECH) on varying the molar ratio of Schiff base complexes of cobalt(II) and nickel(II) ions complexes was same as observed with Schiff base complexes of iron(III) ions, but the selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was higher with Schiff base complexes of iron(III) than Schiff base complexes of cobalt(II) and nickel(II) ions (Table 7). The decrease in product selectivity at a higher molar ratio of catalysts (>1) was due to the significant change in microenvironment on active sites of catalyst on polymer support. The interactions in reaction intermediates with phenol and cyclohexene were influenced significantly on varying the molar ratio of catalyst in the reaction mixture; hence, percent conversion of phenol and cyclohexene varied along with selectivity for catechol and epoxy cyclohexane (ECH). During molar ratio variation of hydrogen peroxide and substrate (phenol/cyclohexene), the selectivity for catechol (CTL) and epoxy cyclohexane (ECH) remained constant (Table 4), which was a clear indication that the interactions of substrates in reaction intermediates (Schemes 7a and b) remained unaffected. The interactions between substrate and catalyst in reaction intermediates were affected adversely at high molar ratio of catalyst (>1); hence, selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was decreased (Table 7) along with the decrease in conversion of phenol (Figure 11) and cyclohexene (Figure 12).

The rate of oxidation of phenol and epoxidation of cyclohexene with supported HPHZ Schiff base complexes of iron(III) ions was $2.13 \times 10^{-6}\,\mathrm{ML^{-1}\,s^{-1}}$ and $2.74 \times 10^{-6}\,\mathrm{ML^{-1}\,s^{-1}}$ respectively, whereas with unsupported HPHZ Schiff base complexes of iron(III) ions, the rate was $1.94 \times 10^{-6}\,\mathrm{ML^{-1}\,s^{-1}}$ and $2.5 \times 10^{-6}\,\mathrm{ML^{-1}\,s^{-1}}$ respectively, which clearly indicated that the activity of the catalyst was influenced by polymer support (Tables 5 and 6). The rate of oxidation of phenol and epoxidation of cyclohexene was low with supported HPHZ Schiff base complexes of cobalt(II) and nickel(II) ions in comparison to iron(III) ions complexes. The turnover number (TON) for oxidation of phenol and epoxidation of cyclohexene was also influenced by the molar ratio of catalyst and found to be optimum at a 1:1:1 molar ratio of catalyst to substrate and oxidant. The turnover number for oxidation of phenol and epoxidation of cyclohexene was high with free and supported Schiff base complexes of iron(III) ions (Tables 5 and 6).

3.4.4 *Effect of Reaction Temperature on Oxidation and Epoxidation*

The energy of activation is a useful parameter to predict the state and interactions of catalysts with the reactants. Therefore, investigations were also carried out to determine the activation energy for the conversion of phenol and cyclohexene in the presence of free and polymer supported HPHZ Schiff base complexes of metal ions. The oxidation of phenol was studied by varying the reaction temperature from 60°C to 80°C, whereas, epoxidation of cyclohexene was studied by varying the reaction temperature from 30°C to 50°C at 1:1:1 molar ratio of phenol/cyclohexene to catalysts and hydrogen peroxide at constant molarity (0.05 M). The rate constants (k) for these reactions were determined at different temperatures and used to calculate the energy of activation. The oxidation of phenol increased on increasing the reaction temperature from 60°C to 70°C and epoxidation of cyclohexene has also shown an increasing trend on increasing the reaction temperature from 30°C to 40°C. However, on further increasing the reaction temperature beyond 70°C and 40°C, the conversion of phenol and cyclohexene was decreased both in presence of unsupported and polymer supported HPHZ Schiff base complexes of metal ions (Table 8).

The decreasing trend at high temperature (>70°C) in conversion of phenol was attributed for the decomposition of hydrogen peroxide without oxidizing phenol and cyclohexene. The decomposition of hydrogen peroxide at high temperature has decreased the formation of an active species (Schemes 7a and b) in the reaction mixture, which caused a

Table 8. Effect of temperature on conversion of phenol (Ph)/cyclohexene (CH) and product selectivity with supported metal complexes (P-HPHZ-M)

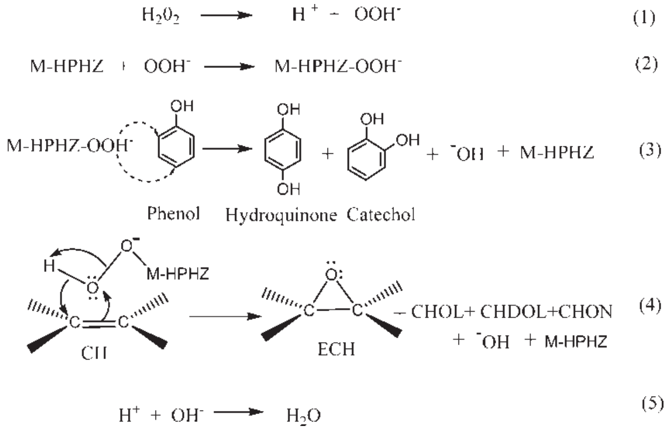
	P-HPHZ-Fe		P-HPHZ-Co		P-HPHZ-Ni	
Temp. (°C)	Ph	CTL	Ph	CTL	Ph	CTL
Phenol conversion (%) and selectivity (%) for catechol (CTL)						
60	42.1	86.1	37.6	84.2	34.2	84.5
70	64.0	90.5	49.0	88.9	57.0	89.3
80	61.4	88.2	45.9	86.3	52.7	87.4
Cyclohexene conversion (%) and selectivity (%) for epoxy cyclohexane (ECH)						
	CH	ECH	CH	ECH	CH	ECH
30	66.4	92.7	51.6	87.5	55.4	90.0
40	81.3	96.5	66.2	92.6	74.7	95.1
50	79.4	94.9	64.8	88.9	71.2	92.5

$[H_2O_2]$:[Catalyst]:[Phenol] = 1:1:1 (0.05 M), Time = 1440 min, CH_3CN = 2.0 mL.

significant decrease in conversion of phenol and cyclohexene. The increase in reaction temperature beyond 70°C and 40°C has also shown a significant decrease in selectivity for catechol (CTL) and epoxy cyclohexane (ECH) in presence of both free and supported HPHZ Schiff base complexes of metal ions (Table 8). The variation in selectivity with reaction temperature was due to the variation in microenvironment in reaction intermediates, which controlled the interactions of reactants with catalysts and a intramolecular electron transfer process before undergoing a process of decomposition to produce reaction products. The nature of these interactions and electron transfer process were responsible for controlling the product selectivity of the reactions. At higher temperatures, these interactions in reaction intermediates were affected adversely; hence, the selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was decreased (Table 8). The rate constant (k) for conversion of phenol and cyclohexene was $4.29 \times 10^{-5}\,s^{-1}$ and $5.0 \times 10^{-5}\,s^{-1}$, respectively in presence of polymer supported HPHZ Schiff base complexes of iron(III) ions whereas, in case of HPHZ Schiff base complexes of cobalt(II) and nickel(II) ions, the value of rate constant (k) was lower than found with Schiff base complexes of iron(III) ions. The value of rate constant (k) increased till 70°C in conversion of phenol and till 40°C in cyclohexene conversion. The further increase in temperature beyond 70°C and 40°C, the value of rate constant decreased both in free and polymer supported Schiff base complexes of metal ions. The increase in the value of rate constant (k) for the conversion of phenol and cyclohexene with reaction temperature was an indication that the oxidation of phenol and epoxidation of cyclohexene are energy activated processes and supported catalysts play a significant role in decreasing the energy of activation for conversion of phenol and cyclohexene. The energy of activation for the oxidation of phenol and epoxidation of cyclohexene in presence of free and supported catalysts was estimated for complexes of iron(III), cobalt(II) and nickel(II) ions (Tables 5 and 6). The energy of activation for conversion of phenol and cyclohexene with polymer supported Schiff base complexes of iron(III) ions was 22.8 kJ mol^{-1} and 8.9 kJ mol^{-1}, respectively, but it was high for the conversion of phenol and cyclohexene in presence of supported Schiff base complexes of cobalt(II) and nickel(II) ions (Tables 5 and 6). The activation energy for these reactions with unsupported HPHZ Schiff base complexes of metal ions was higher than observed with supported Schiff base complexes of metal ions. The electron transfer process in reaction intermediates is (43) an activated process and polymer support has played a significant role in decreasing this energy of activation; hence, the energy of activation for conversion of phenol and cyclohexene was lower with polymer supported Schiff base complexes of metal ions than with free and unsupported metal complexes. The variation in energy of activation with Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions was due to the difference in their structures and electronic configurations, which controlled the interactions and electron transfer process in reaction intermediates (Schemes 7a and b).

3.4.5 *Mechanism for Oxidation and Epoxidation*

Considering the experimental findings for the oxidation of phenol and epoxidation of cyclohexene in presence of free and supported HPHZ Schiff base complexes of metal ions, the following reaction steps (Equations 1–5) are proposed. The ortho and para interactions of active species (HOO-HPHZ-M^-) with phenol were responsible for the formation of catechol and hydroquinone, but selectivity for catechol was due to predominant ortho interactions. These interactions varied with the type of metal ions, their concentration and with reaction temperature.



In the case of cyclohexene, the interactions of active species (M-HPHZ-HOO^-) with cyclohexene produced epoxy cyclohexane (ECH) as a major product and 1,2-cyclohexanediol (CHDOL), 2-cyclohexene-1-one (CHON), 2-cyclohexene-1-ol (CHOL) as minor products. The reaction products, catalyst and hydroxyl ions were formed through equilibrium decomposition of reaction intermediates (Schemes 7a and b) and finally, the hydroxyl ions reacted with hydrogen ions in last step (Equation (5).

4 Conclusions

The polymer supported transition metal complexes of N, N′-bis(o-hydroxy acetophenone) hydrazine (HPHZ) Schiff base were synthesized and characterized successfully for their structures and catalytic activity in oxidation of phenol and epoxidation of cyclohexene. The polymer supported HPHZ Schiff base complexes of metal ions showed high catalytic activity than unsupported metal complexes. The Schiff base complexes of iron(III) ions were more catalytic in conversion of phenol and cyclohexene than cobalt(II) and nickel(II) ions complexes. The oxidation of phenol showed high selectivity for catechol whereas; cyclohexene was selectively oxidized to epoxy cyclohexane. The supported catalysts showed low activation energy in both reactions than unsupported catalysts, which clearly suggested that polymer support has played a significant role in decreasing the energy of activation in these reactions in presence of metal complexes of HPHZ Schiff base.

5 Acknowledgements

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

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