

# Synthesis of Polymer-Supported Metal-Ion Complexes and Evaluation of Their Catalytic Activities

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**ABSTRACT:** Polymer-supported transition-metal-ion complexes of the *N,N'*-bis(*o*-hydroxy acetophenone) propylendiamine (HPPn) Schiff base were prepared by the complexation of iron(III), cobalt(II), and nickel(II) ions on a polymer-anchored *N,N'*-bis(5-amino-*o*-hydroxy acetophenone) propylendiamine Schiff base. The complexation of iron(III), cobalt(II), and nickel(II) ions on the polymer-anchored HPPn Schiff base was 83.44, 82.92, and 89.58 wt %, respectively, whereas the unsupported HPPn Schiff base showed 82.29, 81.18, and 87.29 wt % complexation of these metal ions. The iron(III) ion complexes of the HPPn Schiff base showed octahedral geometry, whereas the cobalt(II) and nickel(II) ion complexes were square planar in shape, as suggested by spectral and magnetic measurements. The thermal stability of the HPPn Schiff base increased with the complexation of metal ions, as evidenced by thermogravimetric analysis. The HPPn Schiff base showed a weight loss of 51.0 wt % at 500°C, but its iron(III), cobalt(II), and nickel(II) ion complexes showed weight losses of 27.0, 35.0, and 44.7 wt % at the same temperature. The catalytic activity of the unsupported and supported metal-ion complexes was analyzed by the study of the oxidation of phenol and epoxidation of cyclohexene in the presence of hydrogen peroxide. The supported

HPPn Schiff base complexes of iron(III) ions showed a 73.0 wt % maximum conversion of phenol and 90.6 wt % epoxidation of cyclohexene, but unsupported complexes of iron(III) ions showed 63.8 wt % conversion of phenol and 83.2 wt % epoxidation of cyclohexene. The product selectivity for catechol (CTL) and epoxy cyclohexane (ECH) was 93.1 wt % and 98.1 wt % with the supported HPPn Schiff base complexes of iron(III) ions, but it was low with the supported Schiff base complexes of cobalt(II) and nickel(II) ions. The selectivity for CTL and ECH varied with the molar ratio of the metal ions but remained unaffected by the molar ratio of hydrogen peroxide to the substrate. The energy of activation for the epoxidation of cyclohexene and oxidation of phenol with the polymer-supported Schiff base complexes of iron(III) ions was 10.0 and 12.7 kJ/mol, respectively, but it was found to be higher with the supported HPPn Schiff base complexes of cobalt(II) and nickel(II) ions and with the unsupported HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3927–3941, 2008

**Key words:** crosslinking; heterogeneous polymers; metal-organic catalysts/organometallic catalysts; metal-polymer complexes; polystyrene

## INTRODUCTION

Schiff base complexes of transition-metal ions have shown significant catalytic activities in various reactions such as oxidation,<sup>1,2</sup> epoxidation of olefins,<sup>3,4</sup> and polymerization of ethylenes,<sup>5,6</sup> but supported metal-ion complexes have shown high catalytic activity<sup>7–9</sup> and enantioselectivity<sup>10,11</sup> in comparison with homogeneous and unsupported catalysts. Cobalt(II) and manganese(II) ion complexes of salen on tailor-made polymer supports have shown considerable increases in activity<sup>9,12</sup> and enantioselectivity<sup>12</sup> due to a significant reduction in the mass-transfer limitation for the reactants. Although metal-ion complexes have been immobilized on various

supports,<sup>13–17</sup> their activity on polymer supports is quite high<sup>18,19</sup> because of the dynamic microenvironment<sup>20</sup> and liquid-phase conditions,<sup>21,22</sup> in which an anchored catalyst is able to perform rotational and translational motions such as homogeneous catalysis. The homogeneity of catalysts on zeolite<sup>23</sup> and silica<sup>24</sup> supports is significantly different from that on polymer supports. Metal-ion complexes on various supports are immobilized either physically<sup>9,25–27</sup> or by the formation of a bond between metal-ion complexes and supports,<sup>27–31</sup> but the recovery of physically linked catalysts is usually low because of the leaching of the catalyst<sup>9,27</sup> in the reaction mixture in comparison with covalently bound catalysts. The Schiff base complexes of metal ions have been used in the oxidation of phenols,<sup>32</sup> but the oxidation of phenol with polymer-supported transition-metal-ion complexes has been found to be higher in the presence of *t*-butyl hydroperoxide.<sup>31,33</sup> Similarly, aluminosilicate-supported polymer-modified complexes of manganese ferrocyanide have shown high catalytic activity in the oxidation of cyclohexene and

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produced cyclohexanone and cyclohexanal in the presence of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as an oxidant.<sup>34</sup> Polymer-supported Schiff base complexes of metal ions have also been used in the decomposition of  $\text{H}_2\text{O}_2$ , in which the catalytic activity is assumed to be dependent on the redox potentials of the metal ions.<sup>35</sup> These investigations are useful in explaining the catalytic activity of metal ions in the oxidation of phenol and cyclohexene in the presence of  $\text{H}_2\text{O}_2$  as an oxidant. Transition-metal-ion complexes also play a significant role in the reduction of the energy of activation of  $\text{H}_2\text{O}_2$ ,<sup>36,37</sup> but polymer-supported metal ion complexes are more active in the reduction of the energy of activation of decomposition of  $\text{H}_2\text{O}_2$  in the oxidation of phenol.<sup>38</sup> Supported catalysts also have shown high catalytic activity in the epoxidation of cyclohexene in the presence of *t*-butyl hydroperoxide<sup>39,40</sup> as an oxidant. The decomposition of  $\text{H}_2\text{O}_2$ <sup>41,42</sup> with polymer-supported complexes of cobalt(II) ions has shown variation with the solution pH, which might be due to the variation in the redox potential of metal ions<sup>35</sup> and degree of swelling in the polymer matrix. Although the oxidation of phenol and epoxidation of cyclohexene with  $\text{H}_2\text{O}_2$  in the presence of metal-ion complexes of salen have been reported, the catalytic activity of metal-ion complexes of the *N,N'*-bis(*o*-hydroxy acetophenone) propylenediamine (HPPn) Schiff base has not been reported in the literature; hence, attempts have been made to synthesize and characterize polymer-supported metal-ion complexes of the HPPn Schiff base and to evaluate their catalytic activity in the oxidation of phenol and cyclohexene in the presence of  $\text{H}_2\text{O}_2$  as an oxidant in comparison with unsupported HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions.

## EXPERIMENTAL

### Materials

Crosslinked polystyrene beads were obtained from Ion Exchange India, Ltd. (Mumbai, India). The chloro salts of iron(III), cobalt(II), and nickel(II) ions were purchased from Ranbaxy (Mumbai, India) and used without further purification. The cyclohexene, phenol,  $\text{H}_2\text{O}_2$  (30 wt %), *o*-hydroxy acetophenone, and propylenediamine were procured from E. Merck (Mumbai, India). Other chemicals and solvents were analytical-grade (>99%) and were used after purification with standard methods.<sup>43</sup>

### Characterization of the Schiff base and its metal-ion complexes

IR spectra of the HPPn Schiff base and its metal-ion complexes were recorded on KBr pellet with a PerkinElmer 1600 Fourier transform infrared spectro-

meter (Norwalk, CT). The electronic spectra of the HPPn Schiff base and its metal-ion complexes were recorded with a Shimadzu 1601 PC ultraviolet-visible spectrophotometer (Tokyo, Japan) with the sample mull kept in a cuvette. Thermogravimetric analysis (TGA) of the HPPn Schiff base and its metal-ion complexes was carried out with a PerkinElmer Pyris diamond thermal analyzer in a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The loading of metal ions onto the HPPn Schiff base was determined by an analysis of the solution with a PerkinElmer 3100 atomic absorption spectrometer at  $\lambda_{\text{max}}$  for each metal ion. The composition and amount of the HPPn Schiff base anchored onto polymer beads were determined by elemental analysis with a Heraeus Carlo Erba 1108 elemental analyzer (Milano, Italy). The  $^1\text{H}$ -NMR spectra of the HPPn Schiff base and its metal-ion complexes were recorded on a Bruker 300-MHz Fourier transform NMR spectrometer (Karlruhe 21, FRG) with dimethyl sulfoxide- $d_6$  as the solvent and tetramethylsilane as the internal reference. The magnetic moment of the metal-ion complexes was measured with a model 155 vibrating sample magnetometer (Princeton, NJ). The molecular weight of the HPPn Schiff base and its metal-ion complexes was determined in dimethyl formamide with a vapor pressure osmometer (K-700, Knauer, Berlin, Germany) and with benzyl as the standard.

### Synthesis of the HPPn Schiff base and its metal-ion complexes

The HPPn Schiff base was synthesized by the modification of the procedure reported in the literature.<sup>43</sup> A mixture of *o*-hydroxy acetophenone (20.0 mmol, 2.22 g) and propylenediamine (10.0 mmol, 0.74 g) in methanol (20.0 mL) was refluxed for 45 min at  $60^\circ\text{C}$ . The reaction mixture on cooling produced light yellow crystals, which were filtered and recrystallized in methanol. The metal-ion complexes of the HPPn Schiff base were prepared by the refluxing of the HPPn Schiff base (20.0 mmol, 6.21 g) and metal ions (20.0 mmol) in methanol (20.0 mL) in a round-bottom flask at  $70^\circ\text{C}$ . After 8 h, the solution was cooled, and crystalline metal-ion complexes were separated from the mother liquor. Finally, the metal-ion complexes were recrystallized in methanol and dried in a vacuum oven at  $60^\circ\text{C}$ .

### Synthesis of the polymer-anchored Schiff base and its metal-ion complexes

To prepare polymer-anchored metal-ion complexes of the HPPn Schiff base, the *N,N'*-bis(5-amino-*o*-hydroxy acetophenone) propylenediamine (AHPPn) Schiff base was prepared through nitrosation and reduction reactions on the HPPn Schiff base and

then the reaction of the synthesized AHPPn Schiff base with chloromethylated polystyrene beads. The nitrosation of the HPPn Schiff base was carried out through the reaction of 20.0 mmol (6.208 g) of the HPPn Schiff base with sodium nitrite (20.0 mmol) in 20.0 mL (1.0N) of hydrochloric acid at  $-5.0^{\circ}\text{C}$ . The resultant *N,N'*-bis(5-nitroso-*o*-hydroxy acetophenone) propylenediamine (NOHPPn) was filtered and washed with hot and cold water to remove the reaction impurities. Subsequently, the reduction of the NOHPPn Schiff base was carried out with 20.0 mmol of the NOHPPn Schiff base in 20.0 mL (1.0N) of hydrochloric acid in the presence of pieces of metallic iron, which produced the AHPPn Schiff base. To immobilize the prepared AHPPn Schiff base on chloromethylated polystyrene beads, 5.0 g of methanol-swollen polymer beads and 20.0 mmol (6.22 g) of the AHPPn Schiff base were refluxed at  $60^{\circ}\text{C}$  in a round-bottom flask containing 20.0 mL of methanol. After 8 h, the HPPn Schiff base anchored polymer beads were separated and dried in a vacuum oven at  $60^{\circ}\text{C}$ . The amount of the HPPn Schiff base loaded on the polymer beads was estimated by elemental analysis. The complexation of metal ions on the polymer-anchored HPPn Schiff base was carried out by HPPn Schiff base anchored polymer beads (5.0 g) being kept in a 20.0-mL solution of metal ions (20.0 mmol) for 10 h. Finally, the polymer beads were separated and dried at  $60^{\circ}\text{C}$  in a vacuum oven after being washed with hot and cold water. The loading of metal ions was determined by the analysis of the loading solution with an atomic absorption spectrometer. The loading of metal ions on the unsupported and polymer-supported HPPn Schiff bases was calculated as the efficiency of complexation with the following equation:

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

#### Catalytic activity of metal-ion complexes in the oxidation of phenol and the epoxidation of cyclohexene

The catalytic activity of the unsupported and polymer-supported metal-ion complexes of the HPPn Schiff base in the oxidation of phenol and epoxidation of cyclohexene was determined with  $\text{H}_2\text{O}_2$  as an oxidant at a fixed ionic strength (0.1M) and solution pH. To study these reactions, a calculated amount of metal-ions-anchored polymer beads was placed in a two-necked, round-bottom flask containing 4.70 g of phenol (0.05M) or 4.10 g of cyclohexene (0.05M) and 2.0 mL of acetonitrile/chlorobenzene as the internal standard. To start the reaction, a calculated volume

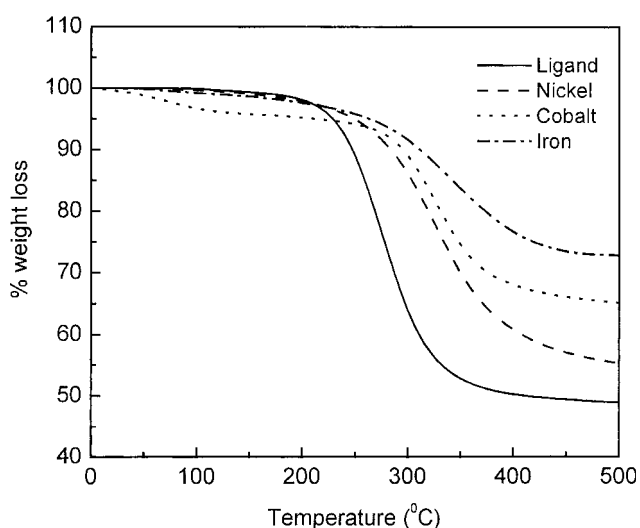
of  $\text{H}_2\text{O}_2$  (30 wt %) was added to maintain a 0.05M concentration of  $\text{H}_2\text{O}_2$  in the reaction mixture. Finally, the water condenser and nitrogen supply were attached to the reaction flask, and the reaction mixture was heated at constant stirring (1200 rpm). To estimate the conversion of phenol and cyclohexene, aliquots of the reaction mixture were taken out at different time intervals and analyzed with the gas chromatography method. To identify the reaction products, the retention times of standards were used, and peak areas in the chromatograms were used to measure product selectivity. To analyze cyclohexene and epoxy cyclohexane (ECH) in the reaction mixture, the gas chromatograph was fitted with a column (1.0 m) packed with W-DMCS chromosorb with a liquid SE-30 phase of about 2.5 wt % and 0.03 wt % poly(ethylene glycol) with a molecular weight of 2000 da (Accuspec, Instrument Corp., Wantagh, NY). The temperatures of the injection port and column were maintained at 150 and  $85^{\circ}\text{C}$ , respectively, and the carrier gas was supplied at 20.0 mL/min. For an analysis of phenol, catechol (CTL), and hydroquinone (HQ), a fused silica capillary column (XE-60; 30 m  $\times$  0.2 mm  $\times$  0.3  $\mu\text{m}$ ) was used (Perkin-Elmer Corp., Norwalk, CT). The temperatures of the injection port and column were maintained at 280 and  $180^{\circ}\text{C}$ , respectively, and the carrier gas was supplied at a rate of 20.0 mL/min. These reactions were also studied at different molar ratios of the substrates,  $\text{H}_2\text{O}_2$ , and catalyst in the reaction mixture and at different temperatures to determine the energy of activation for the oxidation of phenol and epoxidation of cyclohexene. To test the stability of the polymer-anchored metal-ion complexes and leaching of metal ions, the polymer-anchored metal-ion complexes were recycled and reused in these reactions. To analyze the effect of the catalyst on the oxidation of phenol and epoxidation of cyclohexane, the reactions were also studied without catalysts.

## RESULTS AND DISCUSSION

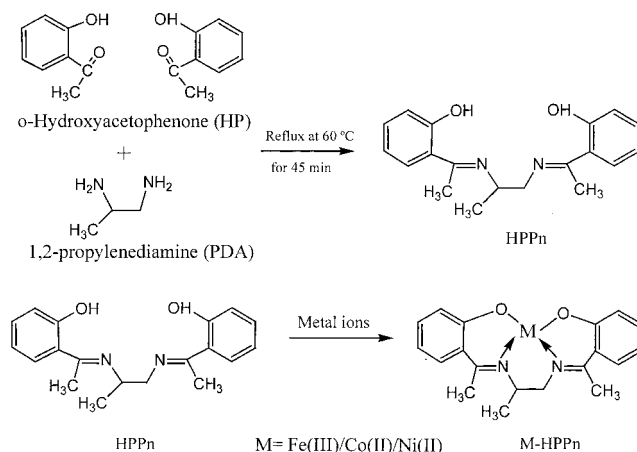
The oxidation of phenol and epoxidation of cyclohexene with polymer-anchored HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions were found to be higher and more selective than those with unsupported HPPn Schiff base complexes of these metal ions. These results clearly indicate that a polymer support plays a positive role in modifying the activity of metal-ion complexes, as reported in the literature.<sup>9,31,44</sup> The activity of a catalyst on a support is increased, provided that the nature of the catalyst is not destroyed and the support is able to provide a liquid-phase environment as found with polymer supports; hence, the properties of polymer supports influence the activity of anchored catalysts.<sup>45</sup> Although the amount of loaded metal

ions<sup>46,47</sup> influences the activity of a supported catalyst, the activity of a supported catalyst is also influenced by leaching of the catalyst from the polymer support.<sup>27</sup> In physically anchored catalysts, the leaching of a catalyst has been assumed to be beneficial for catalysis,<sup>27</sup> but the leaching of a catalyst from a polymer-bound catalyst has been found to be harmful in catalysis as polymer-bound catalysts are able to reveal homogeneous conditions in the matrix and at the surface of polymer supports.<sup>21,22</sup> The leaching of catalysts from the polymer-anchored complexes was determined by an analysis of the recycled catalyst ash for loaded metal ions with an atomic absorption spectrometer, and it was found to be insignificant for polymer-supported catalysts recycled up to six times. The analysis of the recycled catalysts also indicated that the supported catalysts were stable and maintained their catalytic activity in the oxidation of phenol and epoxidation of cyclohexene without leaching of metal ions as found with physically anchored catalysts.<sup>27</sup> The thermal stability of the unsupported and supported catalysts was also analyzed for their applications in high-temperature reactions and to provide proof for the complexation of metal ions with a polymer-anchored Schiff base. TGA of the HPPn Schiff base showed a weight loss of 51.0 wt % at 500°C, but its iron(III), cobalt(II), and nickel(II) ion complexes showed weight losses of 27.0, 35.0, and 44.7 wt %, respectively, at the same temperature; this clearly indicated that iron(III) ion complexes (Fig. 1) were more stable than cobalt(II) and nickel(II) ion complexes. The weight loss at 500°C was attributed to the decomposition of the HPPn Schiff base complexes of metal ions.

The temperature of the maximum rate of decomposition of the polymer-anchored Schiff base



**Figure 1** Thermal stability of the polymer-supported HPPn Schiff base and its metal complexes.



**Scheme 1** Synthesis of the HPPn Schiff base and its metal-ion complexes.

(P-HPPn) was increased from 225 to 325°C on complexation with iron(III) ions and increased to 319 and 281°C on complexation with cobalt(II) and nickel(II) ions, respectively (Fig. 1).

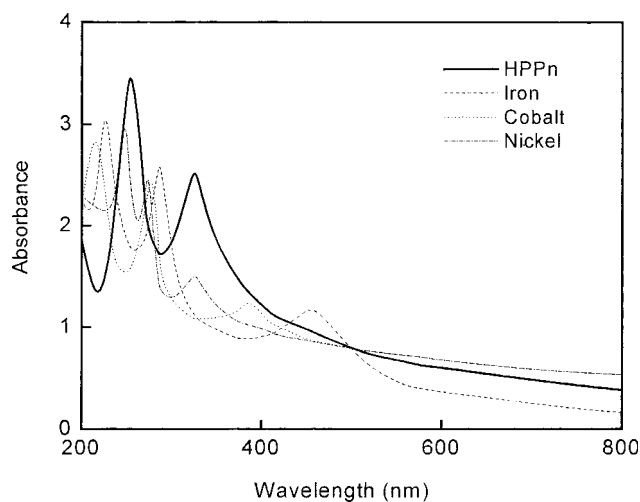
#### Characterization of the HPPn Schiff base

The refluxing of propylenediamine and *o*-hydroxyacetophenone for 45 min at 60°C in methanol produced a substantial yield (86.20 wt %) of the HPPn Schiff base (Scheme 1). The IR spectrum of the HPPn Schiff base showed absorption bands at 1610 ( $>\text{C}=\text{N}$ ) and 1275  $\text{cm}^{-1}$  [ $(>\text{C}-\text{O})_{\text{phenolic}}$ ], and a broad band between 3380 and 2910  $\text{cm}^{-1}$  was also observed, which was assigned to phenolic OH.

The elemental analysis of the HPPn Schiff base showed the following: experimental values of 72.98 wt % C, 8.33 wt % N, and 6.99 wt % H and calculated values of 73.52 wt % C, 9.03 wt % N, and 7.14 wt % H, which corresponded to the  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$  empirical formula of the HPPn Schiff base. The molecular weight of the Schiff base was found to be 310.40 g/mol (calcd 310.30 g/mol). The electronic spectra of the HPPn Schiff base (Fig. 2) showed bands at 255 and 324 nm, which were assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The  $^1\text{H-NMR}$  spectrum of the HPPn Schiff base showed signals at  $\delta$  values of 1.02 (3H), 1.04 (3H), 1.43 (3H), 3.45 (1H), 4.14 (2H), 5.15 (2H), 6.91 (2H), 7.0 (2H), 7.27 (2H), and 7.60 ppm (2H), which corresponded to the structure of the HPPn Schiff base shown in Scheme 1.

#### Synthesis and characterization of the AHPPn Schiff base and its anchoring on polymer supports

The nitrosation of the HPPn Schiff base with  $\text{NaNO}_2/\text{HCl}$  produced 86.49 wt % NOHPPn (Scheme 2). The elemental analysis of NOHPPn showed the following: experimental values of 60.99 wt % C, 14.52 wt % N, and 4.63 wt % H and calculated values of 61.95 wt % C, 15.21 wt % N, and

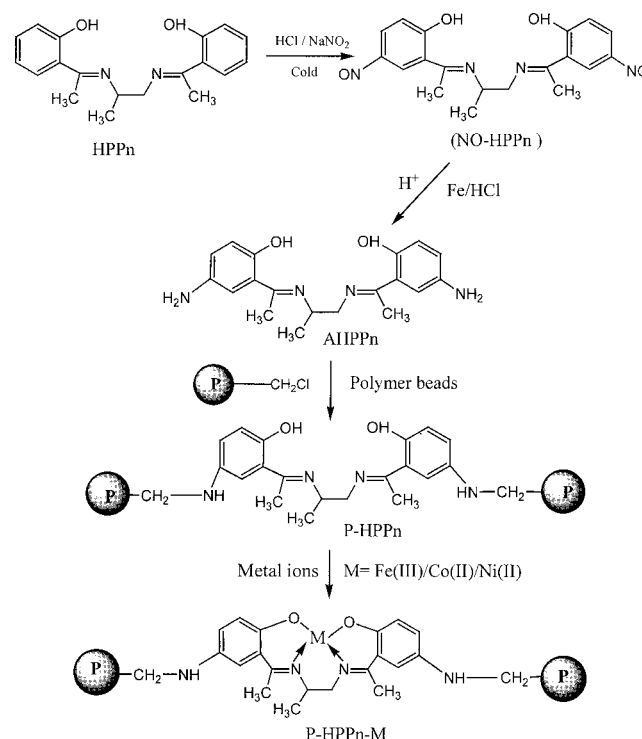


**Figure 2** Electronic spectra of the HPPn Schiff base and its metal complexes.

5.47 wt % H, which corresponded to the  $C_{19}H_{22}N_4O_4$  formula of the nitrosated Schiff base. The molecular weight of NOHPPn was found to be 368.39 g/mol (calcd 368.36 g/mol). The IR spectrum of NOHPPn showed absorption bands at 1630 ( $>C=N$ ), 1280 [ $(>C-O)_{phenolic}$ ], and 1550 and 1335  $cm^{-1}$  for the N—O group. The nitrosation of the HPPn Schiff base showed a shift in the NMR signals in comparison with the NMR signals observed for the pure HPPn Schiff base. The nitrosated HPPn Schiff base showed proton signals at  $\delta$  values of 1.03 (3H), 1.05 (3H), 1.44 (3H), 3.45 (1H), 4.14 (2H), 5.15 (2H), 7.20 (2H), 7.82 (1H), and 8.15 ppm (1H), which corresponded to the structure of the nitrosated HPPn Schiff base shown in Scheme 2. The proton signals ortho to the nitroso group in the HPPn Schiff base were deshielded and hence appeared at 7.82 and 8.15 ppm instead of 7.27 and 7.60 ppm for the pure HPPn Schiff base, and the proton signal at 7.00 ppm was missing because of the substitution of the nitroso group in the benzene. NOHPPn was reduced with iron(III) ions in the presence of hydrochloric acid, which showed an 81.27 wt % yield of the AHPPn Schiff base as shown in Scheme 2. AHPPn was characterized for its melting point, which was 195°C. The elemental analysis of the AHPPn Schiff base showed the following: experimental values of 66.00 wt % C, 15.37 wt % N, and 6.28 wt % H and calculated values of 67.04 wt % C, 16.46 wt % N, and 7.12 wt % H, which corresponded to the  $C_{19}H_{22}N_4O_2$  empirical formula of the Schiff base. The molecular weight of AHPPn was found to be 340.43 g/mol (calcd 340.40 g/mol). The IR spectrum of AHPPn showed absorption bands at 1621 ( $>C=N$ ) and 1268 [ $(>C-O)_{phenolic}$ ] and a band between 1633 and 1650  $cm^{-1}$  ( $>C-N$ ). The  $^1H$ -NMR spectrum of the AHPPn Schiff base showed proton

signals at  $\delta$  values of 1.02 (3H), 1.04 (3H), 1.42 (3H), 3.45 (1H), 4.14 (2H), 5.15 (2H), 6.47 (2H), 6.65 (2H), and 6.80 ppm (2H), which corresponded to the structure of the AHPPn Schiff base as shown in Scheme 2. The synthesized AHPPn Schiff base was anchored on divinyl benzene crosslinked chloromethylated polystyrene beads by the refluxing of the AHPPn Schiff base with polymer beads in dimethylformamide for 8 h at 60°C. The amount of the AHPPn Schiff base anchored on polymer beads was found to be 87 wt %, which corresponded to 3.48 mmol of the AHPPn Schiff base on 1.0 g of polymer beads (Scheme 2).

The anchoring of AHPPn on polymer beads was confirmed by a comparison of the IR spectrum of the HPPn Schiff base anchored polymer beads with the IR spectrum of pure polymer beads. The IR spectrum of the polymer-anchored HPPn Schiff base showed new absorption bands at 1602 ( $>C=N$ ) and 1269  $cm^{-1}$  [ $(>C-O)_{phenolic}$ ] and a broad band between 2895 and 3350  $cm^{-1}$  ( $>C-N$ ), which were absent in the IR spectrum of the pure polymer beads but appeared in the spectrum of the unsupported HPPn Schiff base. The IR spectrum of the pure polymer beads showed an absorption band at 1262  $cm^{-1}$ , which was attributed to the C—Cl bond of chloromethyl present in the crosslinked polymer beads. The decrease in the intensity of the absorption band at 1262  $cm^{-1}$  in the HPPn Schiff base anchored polymer beads was evidence for the anchoring of the



**Scheme 2** Synthesis of the polymer-supported HPPn Schiff base and its metal-ion complexes.

**TABLE I**  
**Efficiency of the Complexation of Metal Ions (wt %)**  
**on an Unsupported Schiff Base (HPPn) and a**  
**Polymer-Supported Schiff Base (P-HPPn)**

Schiff base	Iron(III) ions	Cobalt(II) ions	Nickel(II) ions
HPPn	82.29	81.18	87.29
P-HPPn	83.44	82.92	89.58

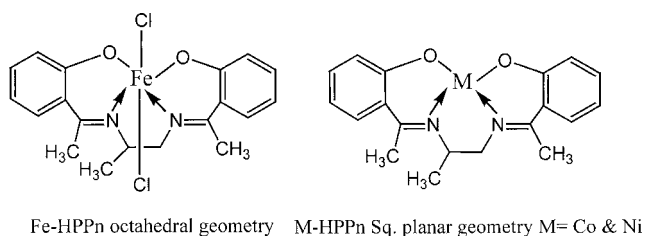
HPPn Schiff base on the polymer beads. The appearance of new absorption bands and shifts in the characteristic absorption bands of the HPPn Schiff base were also used as evidence for the anchoring of the HPPn Schiff base on the polymer beads.

#### Characterization of unsupported and polymer-supported metal-ion complexes of the *N,N'*-HPPn Schiff base

The efficiency of complexation of metal ions on unsupported and polymer-supported HPPn Schiff bases was determined through the refluxing of the HPPn Schiff base (Scheme 1) and polymer-anchored Schiff base in a solution of metal ions at 60°C for 6 h (Scheme 2). The metal-ion complexes of the unsupported HPPn Schiff base (HPPn-M) and polymer-anchored HPPn Schiff base (P-HPPn-M) after separation and purification were characterized for their structures and efficiency for metal-ion complexation. The efficiency of complexation of iron(III) ions on the unsupported HPPn Schiff base and polymer-anchored HPPn Schiff base was 82.29 and 83.44 wt %, respectively (Table I), whereas the efficiency of complexation of cobalt(II) ions on the unsupported and polymer-supported HPPn Schiff base was 81.18 and 82.92 wt %, respectively. The efficiency of complexation of nickel(II) ions was 87.29 wt % on the unsupported HPPn Schiff base and 89.58 wt % on the polymer-anchored HPPn Schiff base, which was higher than that shown by iron(III) and cobalt(II) ions.

These results clearly indicated that the efficiency of complexation of metal ions on the polymer-supported HPPn Schiff base was higher than that on the unsupported HPPn Schiff base. The complexation of metal ions on the HPPn Schiff base showed a significant variation in the IR bands corresponding to  $>C=N$  and  $>C-O$  groups, and new absorptions bands appeared because of the formation of  $M-O$  and  $M-N$  bonds in Schiff base complexes of metal ions. The disappearance of the phenolic absorption band at  $1269\text{ cm}^{-1}$  on complexation of the HPPn Schiff base with metal ions provided evidence for metal-ion complexation with the HPPn Schiff base. The polymer-supported Schiff base showed absorption bands at a low frequency in comparison with the unsupported Schiff base. On complexation with

iron(III) ions with the unsupported HPPn Schiff base, the frequency of the absorption band corresponding to the  $>C=N$  group was shifted from  $1610$  to  $1604\text{ cm}^{-1}$ , whereas it was shifted from  $1602$  to  $1581\text{ cm}^{-1}$  in the polymer-supported HPPn Schiff base. The complexation of cobalt(II) and nickel(II) ions with the polymer-supported HPPn Schiff base showed absorption bands at  $1600$  and  $1578\text{ cm}^{-1}$  in place of  $1602\text{ cm}^{-1}$ . These variations in the IR band corresponding to the  $>C=N$  group of the Schiff base provided evidence for the interactions of metal ions with azomethine nitrogen ( $>C=N$ ) of the HPPn Schiff base. The complexation of iron(III) ions showed a new absorption band at  $488\text{ cm}^{-1}$  with the unsupported HPPn Schiff base and at  $480\text{ cm}^{-1}$  with the polymer-supported HPPn Schiff base, which was due to the formation of the  $M-N$  bond between the iron(III) ions and HPPn Schiff base. The complexation of cobalt(II) ions showed an absorption band at  $440$  and  $432\text{ cm}^{-1}$  for the  $M-N$  bond with the unsupported and polymer-supported Schiff base, whereas the complexation of nickel(II) ions with the unsupported and polymer-supported Schiff base showed absorption bands at  $460$  and  $453\text{ cm}^{-1}$ , respectively, for  $M-N$  bond formation. The complexation of iron(III), cobalt(II), and nickel(II) ions also showed another new band due to the formation of a bond between the metal ions and phenolic oxygen ( $-O-M$ ). The complexation of iron(III), cobalt(II), and nickel(II) ions with the polymer-anchored HPPn Schiff base showed absorption bands at  $539$ ,  $534$ , and  $556\text{ cm}^{-1}$ , respectively, for the  $M-O$  bond. The complexation of metal ions with the HPPn Schiff base was further confirmed by a comparison of the electronic spectra of metal-ion complexes with the electronic spectra of the pure HPPn Schiff base (Fig. 2). The complexation of iron(III) ions with the HPPn Schiff base showed variations in the  $\pi \rightarrow \pi^*$  transitions from  $255$  to  $225\text{ nm}$ , but in the case of cobalt(II) and nickel(II) ions, the  $\pi \rightarrow \pi^*$  transitions appeared at  $215$  and  $248\text{ nm}$ , respectively. The  $n \rightarrow \pi^*$  transitions of the HPPn Schiff base changed from  $324$  to  $287\text{ nm}$  on complexation with iron(III) ions, whereas in the case of cobalt(II) and nickel(II) ions, the  $n \rightarrow \pi^*$  transitions took place at  $277$  and  $273\text{ nm}$ , respectively. The charge transfer (CT) and  $d \rightarrow d$  transitions were also used as evidence for the complexation of metal ions with the HPPn Schiff base. The complexation of cobalt(II) and nickel(II) ions with the HPPn Schiff base showed CT transitions at  $387$  and  $328\text{ nm}$ , but the complexation of iron(III) ions showed no CT transition. The complexation of iron(III), cobalt(II), and nickel(II) ions with the HPPn Schiff base showed  $d \rightarrow d$  transitions at  $459$ ,  $436$ , and  $414\text{ nm}$ , respectively, which indicated  $t_{2g}^5 e_g^0$ ,  $t_{2g}^6 e_g^1$ , and  $t_{2g}^6 e_g^2$  electronic configurations for iron(III), cobalt(II), and nickel(II) ions in these Schiff base com-



**Scheme 3** Geometry and structures of the metal-ion complexes of the HPPn Schiff base.

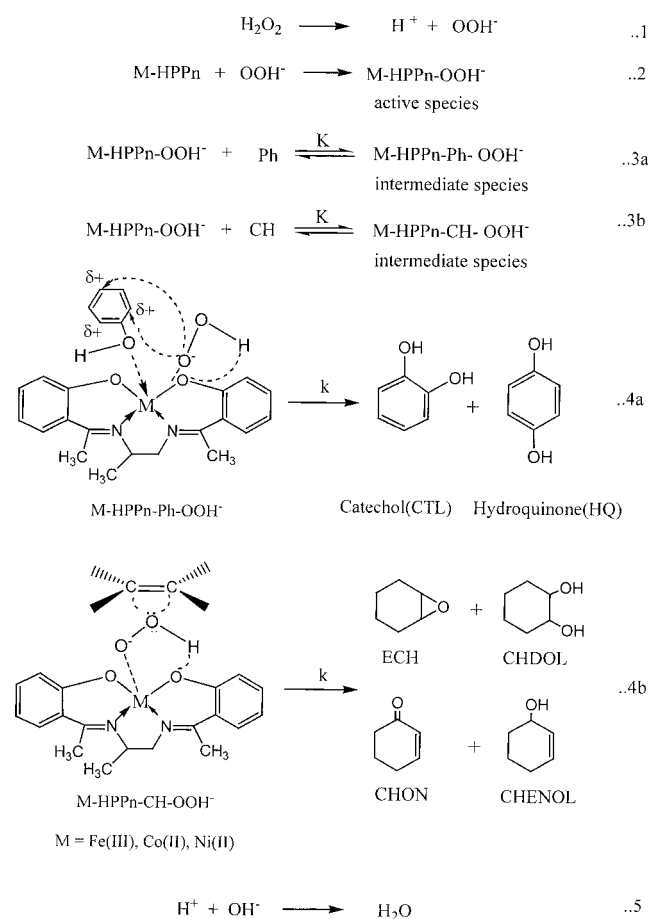
plexes. The magnetic moment of the HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions was found to be 1.87, 1.84, and 0.0 BM, respectively, and this indicated that iron(III) and cobalt(II) ion complexes were paramagnetic in nature with one unpaired electron in each and that nickel(II) ion complexes were diamagnetic in nature with all paired electrons. The magnetic moment and electronic configurations of the metal ions in these complexes suggested octahedral geometry for Schiff base complexes of iron(III) ions with  $d^2sp^3$  hybridization and square planar geometry for cobalt(II) and nickel(II) ions with  $dsp^2$  hybridization (Scheme 3).

### Oxidation of phenol and epoxidation of cyclohexene

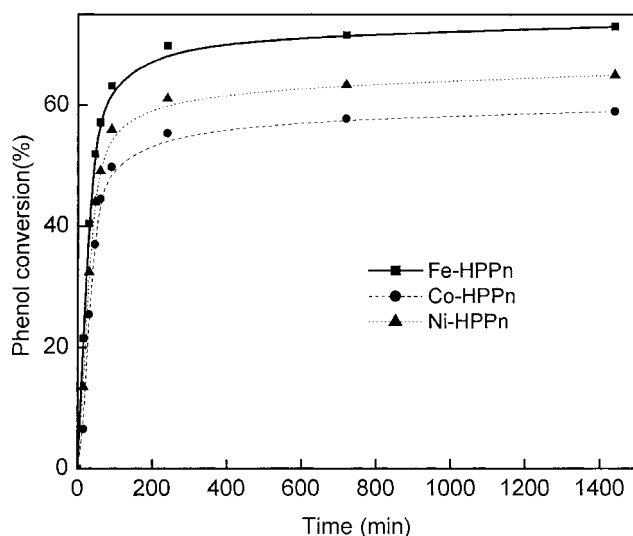
The catalytic activity of unsupported and polymer-supported metal-ion complexes of the HPPn Schiff base was evaluated by the study of the oxidation of phenol and epoxidation of cyclohexene in the presence of  $H_2O_2$ . The product selectivity and conversion (%) of phenol and cyclohexene were estimated successfully by a gas chromatography technique. CTL was a major reaction product in the oxidation of phenol (step 4a, Scheme 4), and ECH was a major reaction product in the epoxidation of cyclohexene (step 4b, Scheme 4). The formation of reaction products was attributed to the enzymatic behavior of metal-ion complexes of the HPPn Schiff base. The unsupported and polymer-supported HPPn Schiff base complexes of metal ions (HPPn-M) produced an active species ( $M-HPPn-OOH^-$ ) by the interactions of  $H_2O_2$  and the HPPn Schiff base in a fast reaction (step 2, Scheme 4). This active species subsequently produced an intermediate ( $M-HPPn-Ph-OOH^-$  or  $M-HPPn-CH-OOH^-$ ) through interactions of phenol or cyclohexene in a rapid equilibrium step ( $K$ ; step 3, Scheme 4). The intermediate  $M-HPPn-Ph-OOH^-$  facilitated the nucleophilic attack of  $OOH^-$  species on the ortho and para positions on phenol to produce hydroxy-substituted phenols, but selectivity for CTL was due to predominant ortho interactions of  $OOH^-$  with phenol (step 4a, Scheme 4). The interactions in intermediate  $M-HPPn-CH-OOH^-$  assisted with the transfer of oxygen to produce ECH and other reaction products [2-cyclo-

hexene-1-ol (CHOL), 1,2-cyclohexanediol (CHDOL), and 2-cyclohexene-1-one (CHON)] through a slow reaction step (rate constant  $k$ ; step 4b, Scheme 4) in the epoxidation of cyclohexene. Finally, the hydroxyl ions reacted with hydrogen ions produced in step 1 (Scheme 4). The interactions in the intermediate varied with the types of metal ions, their concentration, and the reaction temperature. The decomposition of intermediates was facilitated by the polymer support; so the conversion (%) of phenol and cyclohexene was greater with polymer-supported metal-ion complexes (Figs. 3 and 4) in comparison with unsupported metal-ion complexes of the HPPn Schiff base (Table II).

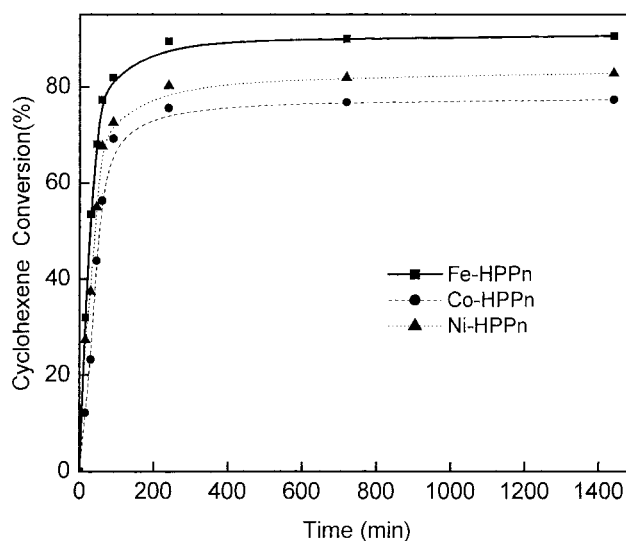
The conversion of phenol and cyclohexene showed an increasing trend up to 240 min, and thereafter, the conversion of phenol and cyclohexene became almost constant; this was due to a substantial decrease in the concentration of the oxidant and substrate in the reaction mixture (Table II). Similar trends for the substrate conversion were also observed with supported catalysts at different time intervals (Figs. 3 and 4). The conversion of phenol and cyclohexene clearly indicated that the oxidation and epoxidation reactions were also dependent on



**Scheme 4** Oxidation of phenol (Ph) and epoxidation of cyclohexene (CH).



**Figure 3** Effect of the reaction time on the oxidation of phenol (Ph) in the presence of polymer-supported metal complexes  $\{[\text{Ph}]/[\text{Catalyst}]/[\text{H}_2\text{O}_2] = 1 : 1 : 1 (0.05\text{M})$  and temperature =  $70^\circ\text{C}$ .



**Figure 4** Effect of the reaction time on the epoxidation of cyclohexene (CH) in the presence of polymer-supported metal complexes  $\{[\text{CH}]/[\text{Catalyst}]/[\text{H}_2\text{O}_2] = 1 : 1 : 1 (0.05\text{M})$  and temperature =  $40^\circ\text{C}$ .

the type of catalyst used in these reactions (Table II). The conversion (%) of phenol and cyclohexene was greater with the HPPn Schiff base complexes of iron(III) ions in comparison with the HPPn Schiff base complexes of cobalt(II) and nickel(II) ions.

The high catalytic activity of metal-ion complexes of the HPPn Schiff base on the polymer support was due to suitable interactions of the catalyst and substrate on the polymer support in comparison with the interactions of the substrate with unsupported catalysts. The low activity of the catalyst in the solution phase was due to the formation of inactive dimers or multimers of metal-ion complexes in the solution. The amount of phenol oxidized with  $\text{H}_2\text{O}_2$  was almost equal to the amount of CTL and HQ; hence, the formation of other reaction products such as polymeric phenols was discarded.

Although the oxidation of phenol produced CTL and HQ, these catalysts showed high selectivity for CTL (Scheme 4). Similarly, the oxidation of cyclohexene produced CHDOL, CHON, and CHOL as reaction products, but ECH was a major product with unsupported and supported catalysts (Scheme 4). However, the product selectivity was greater with supported catalysts. The supported catalysts were reused to evaluate their stability and variation in the activity and selectivity of the products in the oxidation of phenol and epoxidation of cyclohexene. The efficiency of supported catalysts in the conversion of phenol and cyclohexene was almost constant up to six recyclings, and thereafter, the catalysts showed a decreasing trend in their catalytic activity (Table III).

The fresh and recycled catalysts showed higher efficiency in the epoxidation of cyclohexene than in

the oxidation of phenol (Table III), but selectivity for CTL and ECH remained unaffected in recycled catalysts; this was an indication that the metal-ion complexes on the polymer support were quite stable and retained their structures up to six recyclings. The structural stability of the metal-ion complexes on the polymer support was verified by a comparison of the IR spectra of recycled catalysts with IR spectra of freshly prepared catalysts. The catalytic activity of the HPPn Schiff base complexes of metal ions was evaluated under different experimental conditions to optimize their activity and selectivity in the oxidation of phenol and epoxidation of cyclohexene; hence, these reactions were studied with different molar ratios of the reactants and also with different

**TABLE II**  
Catalytic Activity of Unsupported Metal Complexes (M-HPPn) in the Oxidation of Phenol (Ph) and the Epoxidation of Cyclohexene (CH)

Time (min)	Conversion (wt %)					
	Fe-HPPn		Co-HPPn		Ni-HPPn	
	Ph	CH	Ph	CH	Ph	CH
0	0	0	0	0	0	0
15	12.8	25.7	4.5	16.2	7.5	19.3
30	25.7	45.4	11.6	29.6	14.7	28.2
45	36.5	60.9	21.6	39.4	23.8	41.3
60	45	68.2	27.5	49.8	31.5	52.9
90	53.2	76.3	34.1	57.6	50.4	59.5
240	61.7	81.4	45.7	64.5	55.6	66
720	63.3	82.8	48.2	67.3	57	69.3
1440	63.8	83.2	49.2	68.6	58.1	70.9

$[\text{H}_2\text{O}_2]/[\text{Catalyst}]/[\text{Ph}]/[\text{CH}] = 0.05\text{M}$ ; temperature =  $70^\circ\text{C}$  (Ph) or  $40^\circ\text{C}$  (CH).



**TABLE III**  
Efficiency of Recycled Supported Catalysts (P-HPPn-M) in the Oxidation of Phenol (Ph) and the Epoxidation of Cyclohexene (CH)

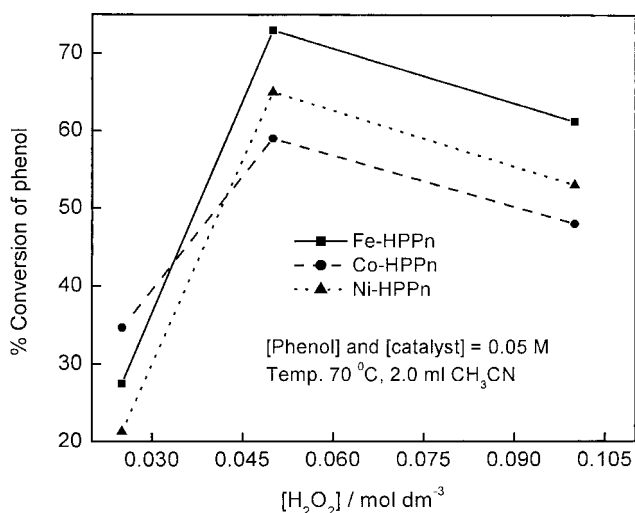
Cycle no.	P-HPPn-Fe	P-HPPn-Co	P-HPPn-Ni
Conversion of Ph (wt %)			
0	73.0	59.0	65.0
2	73.0	59.0	65.0
4	73.0	58.9	65.0
6	72.6	58.7	64.8
8	69.5	54.3	62.4
10	64.9	50.1	59.4
Conversion of CH (wt %)			
0	90.6	77.3	82.8
2	90.6	77.3	82.8
4	90.5	77.1	82.8
6	90.1	76.2	82.2
8	85.8	71.4	79.4
10	81.2	68.4	75.3

$[\text{H}_2\text{O}_2]/[\text{Ph}]/[\text{CH}] = 0.05\text{M}$ ; time = 1440 min; temperature = 70 (Ph) or 40°C (CH);  $\text{CH}_3\text{CN} = 2.0$  mL.

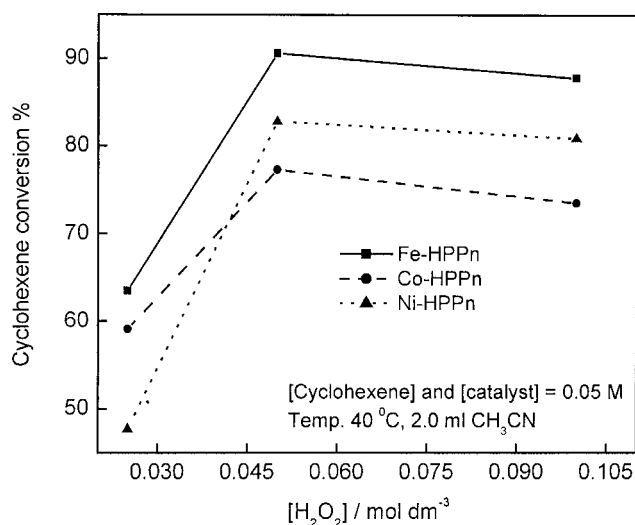
temperatures to evaluate the energy of activation for the oxidation of phenol and epoxidation of cyclohexene with unsupported and supported catalysts.

#### Effect of the $\text{H}_2\text{O}_2$ concentration on the oxidation of phenol and the epoxidation of cyclohexene

The oxidation of phenol and epoxidation of cyclohexene were studied with the variation of the molar ratio of  $\text{H}_2\text{O}_2$  to phenol from 0.5 to 2.0 at a constant molarity of the substrate and catalyst (0.05M) in acetonitrile (2.0 mL). The reaction temperature was maintained at 40°C in the epoxidation of cyclohexene and at 70°C in the oxidation of phenol. When the molar ratio of  $\text{H}_2\text{O}_2$  was varied from 0.5 to 1.0,



**Figure 5** Effect of the  $\text{H}_2\text{O}_2$  concentration on the phenol (Ph) conversion  $[\text{Ph}]/[\text{Catalyst}] = 1 : 1$  (0.05M) and temperature = 70°C).



**Figure 6** Effect of the  $\text{H}_2\text{O}_2$  concentration on the cyclohexene (CH) conversion  $[\text{CH}]/[\text{Catalyst}] = 1 : 1$  (0.05M) and temperature = 40°C).

the oxidation of phenol and epoxidation of cyclohexene increased in the presence of supported HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions (Figs. 5 and 6). However, when the molar ratio of  $\text{H}_2\text{O}_2$  was further increased ( $>1$ ) in the reaction mixture, the oxidation of phenol and epoxidation of cyclohexene showed a decreasing trend, and a similar trend was observed with unsupported HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions. The decreasing trend in the conversion of phenol and cyclohexene at a high molar ratio of  $\text{H}_2\text{O}_2$  ( $>1$ ) was attributed to the decrease in the molar ratio of phenol/cyclohexene to the catalyst in the reaction mixture in comparison with the molar ratio of  $\text{H}_2\text{O}_2$ .

These studies clearly indicated that the HPPn Schiff base complexes of iron(III) ions were more catalytic in the oxidation of phenol (Fig. 5) and epoxidation of cyclohexene (Fig. 6) than the HPPn Schiff base complexes of cobalt(II) ions.

During the molar ratio variation of  $\text{H}_2\text{O}_2$ , the selectivity for CTL and ECH was almost constant in the presence of these Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions (Table IV). During the molar ratio variation of  $\text{H}_2\text{O}_2$ , the average selectivity for CTL was around 93.0 wt % and the average selectivity for ECH was around 98.0 wt % in the presence of HPPn Schiff base complexes of iron(III) ions, which was significantly higher in comparison with the oxidation of phenol<sup>38</sup> and epoxidation of cyclohexene<sup>48,49</sup> reported by other workers.

In the oxidation of phenol, the HPPn Schiff base complexes of cobalt(II) ions showed the lowest selectivity for CTL (92.0 wt %), whereas the HPPn Schiff base complexes of nickel(II) ions showed the lowest selectivity (89.0 wt %) in the epoxidation of cyclo-

**TABLE IV**  
**Product Selectivity at Different Concentrations of Phenol (Ph) or Cyclohexene (CH) and H<sub>2</sub>O<sub>2</sub>**

Molarity (M)	P-HPPn-Fe	P-HPPn-Co	P-HPPn-Ni
Selectivity of CTL in the oxidation of Ph (wt %)			
[H <sub>2</sub> O <sub>2</sub> ]			
0.025	93.2	91.5	91.8
0.050	93.1	91.5	91.9
0.100	93.1	91.4	91.7
[Ph]			
0.025	93.1	91.0	91.9
0.050	93.1	91.5	91.9
0.100	93.0	91.5	91.8
Selectivity of ECH in the oxidation of CH (wt %)			
[H <sub>2</sub> O <sub>2</sub> ]			
0.025	98.0	92.7	89.2
0.050	98.1	92.8	89.2
0.100	98.0	92.8	89.1
[CH]			
0.025	98.1	92.6	89.1
0.050	98.1	92.8	89.2
0.100	98.0	92.7	89.2

[Catalyst] = 0.05M; temperature = 70 (Ph) or 40°C (CH); time = 1440 min; CH<sub>3</sub>CN = 2.0 mL.

hexene. The HPPn Schiff base complexes of metal ions showed higher selectivity for ECH than CTL, and this clearly indicated that the HPPn Schiff base complexes of metal ions were more efficient in the selective epoxidation of cyclohexene than the oxidation of phenol. The rate of phenol conversion (R<sub>p</sub>) was higher ( $2.54 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ ) with HPPn Schiff base complexes of iron(III) ions than with HPPn Schiff base complexes of cobalt(II) ( $2.05 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ ) and nickel(II) ions ( $2.26 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ ; Table V). The rate of phenol conversion and selectivity for CTL were low with unsupported HPPn Schiff base complexes of metal ions.

In the case of the epoxidation of cyclohexene, the rate of cyclohexene conversion was high ( $3.15 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ ) with HPPn Schiff base complexes of iron(III) ions and low ( $2.68 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ ) with HPPn Schiff base complexes of cobalt(II) ions (Table

VI). The turnover number (TON) for the oxidation of phenol was higher ( $17.12 \text{ g mol}^{-1} \text{ Fe h}^{-1}$ ) with HPPn Schiff base complexes of iron(III) ions than with HPPn Schiff base complexes of cobalt(II) ( $13.86 \text{ g mol}^{-1} \text{ Co h}^{-1}$ ) and nickel(II) ions ( $15.28 \text{ g mol}^{-1} \text{ Ni h}^{-1}$ ; Table V).

TON values of unsupported and supported Schiff base complexes of metal ions in the epoxidation of cyclohexene were higher (Table VI) than TON values shown by Schiff base complexes of metal ions in the oxidation of phenol (Table V). The molar ratio variation of H<sub>2</sub>O<sub>2</sub> showed a significant effect on the rate of oxidation of phenol and epoxidation of cyclohexene (Tables V and VI), but selectivity for CTL and ECH remained almost constant (Table IV).

#### Effect of the substrate concentration on oxidation and epoxidation

The catalytic efficiency of the HPPn Schiff base metal-ion complexes in the oxidation of phenol and epoxidation of cyclohexene was evaluated at different molar ratios of phenol and cyclohexene in the reaction mixture, whereas the molar ratio of H<sub>2</sub>O<sub>2</sub> to the catalyst was kept constant. The molar ratio of phenol/cyclohexene was varied from 0.5 to 2.0 with respect to the molar ratio of H<sub>2</sub>O<sub>2</sub> to the catalyst. During the molar ratio variation of phenol/cyclohexene, the concentration of H<sub>2</sub>O<sub>2</sub> and the catalyst was kept constant (0.05M). When the molar ratio of phenol/cyclohexene was increased from 0.5 to 1.0 in the reaction mixture, the conversion (%) of phenol/cyclohexene increased substantially with polymer-supported metal-ion complexes of the HPPn Schiff base (Figs. 7 and 8), but when the molar ratio of phenol/cyclohexene increased further (>1), the conversion (%) of phenol/cyclohexene showed a decreasing trend (Figs. 7 and 8), which was due to the significant decrease in the molar ratio of H<sub>2</sub>O<sub>2</sub> to the catalyst in the reaction mixture in comparison with the molar ratio of phenol/cyclohexene. The conversion (%) of phenol/cyclohexene was maximum at 1 : 1 : 1 molar ratios of phenol/cyclohexene

**TABLE V**  
**Kinetic Parameters for the Oxidation of Phenol (Ph) and Selectivity for CTL**

Catalyst	Conversion (wt %)	Selectivity (wt %)	R <sub>p</sub> × 10 <sup>6</sup> (M L <sup>-1</sup> s <sup>-1</sup> )	TON [g mol (M) <sup>-1</sup> h <sup>-1</sup> ]	Activation energy (kJ/mol)
With unsupported catalysts (HPPn-M)					
HPPn-Fe	63.8	91.2	2.22	14.98	21.2
HPPn-Co	49.2	89.8	1.71	11.56	54.8
HPPn-Ni	58.1	90.2	2.02	13.65	44.0
With supported catalysts (P-HPPn-M)					
P-HPPn-Fe	73.0	93.1	2.54	17.12	12.7
P-HPPn-Co	59.0	91.5	2.05	13.86	49.4
P-HPPn-Ni	65.0	91.9	2.26	15.28	39.2

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

TABLE VI  
Kinetic Parameters for the Epoxidation of Cyclohexene (CH) and Selectivity for ECH

Catalyst	Conversion (wt %)	Selectivity (wt %)	$R_p \times 10^6$ ( $M L^{-1} s^{-1}$ )	TON [g mol (M) <sup>-1</sup> h <sup>-1</sup> ]	Activation energy (kJ/mol)
With unsupported catalysts (HPPn-M)					
HPPn-Fe	83.2	93.0	2.89	17.06	16.6
HPPn-Co	68.6	92.0	2.38	14.06	24.0
HPPn-Ni	70.9	94.0	2.46	14.53	18.5
With supported catalysts (P-HPPn-M)					
P-HPPn-Fe	90.6	98.1	3.15	18.57	10.0
P-HPPn-Co	77.3	92.8	2.68	15.84	15.3
P-HPPn-Ni	82.8	89.2	2.88	16.98	11.8

$[H_2O_2]/[Catalyst]/[CH] = 0.05M$ ; time = 1440 min; temperature = 40°C;  $CH_3CN = 2.0 mL$ .

to  $H_2O_2$  to the catalyst in the reaction mixture. When the molar ratio of phenol/epoxy cyclohexene was varied in the reaction mixture, the conversion (%) of phenol/epoxy cyclohexene was influenced significantly, but selectivity for CTL and ECH remained constant (Table IV). During the molar ratio variation of phenol, the average selectivity for CTL was around 93.0 wt % with the HPPn Schiff base complex of iron(III) ions and between 91.33 and 91.86 wt % with the HPPn Schiff base complexes of cobalt(II) and nickel(II) ions (Table IV). The HPPn Schiff base complexes of metal ions showed similar trends for the selectivity of ECH during the molar ratio variation of cyclohexene, and this clearly indicated that the mechanism of electron transfer in the intermediates  $M-HPPn-Ph-OOH^-$  and  $M-HPPn-CH-OOH^-$  (Schemes 4) remained the same when the molar ratio of phenol/cyclohexene varied and when the molar ratio of  $H_2O_2$  in the reaction mixture varied; hence, selectivity for CTL/ECH was constant when the molar ratio of  $H_2O_2$  to the substrates was varied (Table IV).

The higher conversion (%) and selectivity in the epoxidation of cyclohexene by HPPn Schiff base complexes of metal ions in comparison with the oxidation of phenol was due to the lower energy of activation for the intramolecular electron-transfer process for the decomposition of intermediate  $M-HPPn-CH-OOH^-$  in the epoxidation of cyclohexene (Scheme 4) than for the intramolecular electron-transfer process in the intermediate  $M-HPPn-Ph-OOH^-$  of the oxidation of phenol (Scheme 4). When the molar ratio of phenol/cyclohexene increased from 0.5 to 1.0, the rate of oxidation of phenol and epoxidation of cyclohexene was increased. The rate of phenol oxidation was maximum ( $2.54 \times 10^{-6} M L^{-1} s^{-1}$ ) at a 1 : 1 : 1 molar ratio of phenol,  $H_2O_2$ , and Schiff base complex of iron(III) ions in comparison with HPPn Schiff base complexes of cobalt(II) and nickel(II) ions (Table V). Similarly, the rate of epoxidation of cyclohexene was also maximum ( $3.15 \times 10^{-6} M L^{-1} s^{-1}$ ) at a 1 : 1 : 1 molar ratio of cyclohexene,  $H_2O_2$ , and HPPn Schiff base complex of iron(III) ions in comparison with

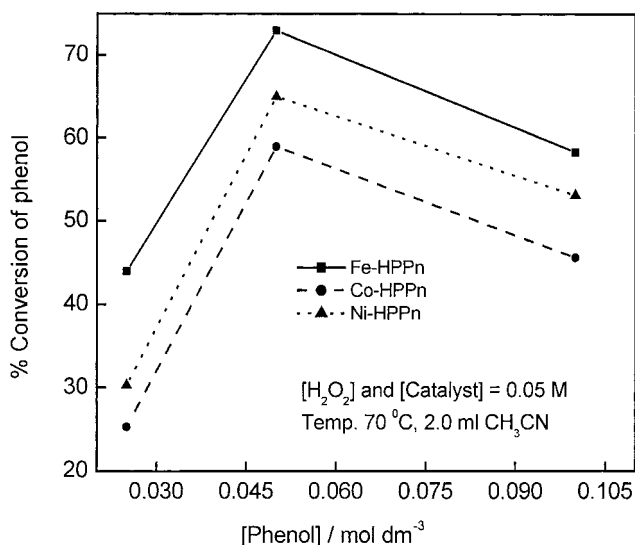


Figure 7 Effect of the phenol concentration on its oxidation {  $[H_2O_2]/[Catalyst] = 1 : 1$  (0.05M) and temperature = 70°C}.

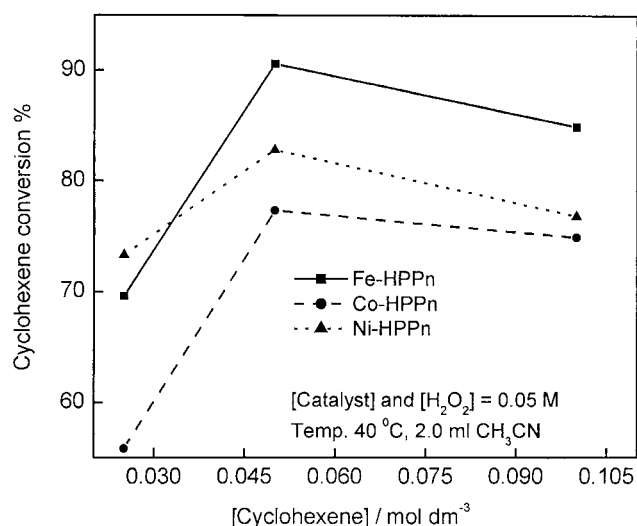


Figure 8 Effect of the cyclohexene concentration on its epoxidation {  $[H_2O_2]/[Catalyst] = 1 : 1$  (0.05M) and temperature = 40°C}.

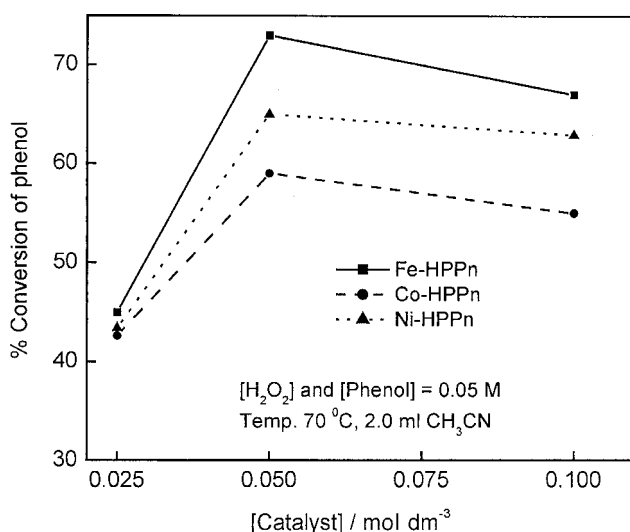
HPPn Schiff base complexes of cobalt(II) and nickel(II) ions (Table VI).

The rate of oxidation of phenol and epoxidation of cyclohexene was found to be lowest with HPPn Schiff base complexes of cobalt(II) ions at a 1 : 1 : 1 molar ratio of the substrate,  $H_2O_2$ , and catalyst (Tables V and VI). TON increased with the increase in the molar ratio of phenol/cyclohexene in the reaction mixture and was found to be maximum at a 1 : 1 : 1 molar ratio of phenol/cyclohexene,  $H_2O_2$ , and the catalyst (Tables V and VI), and HPPn Schiff base complexes of iron(III) ions showed the highest TON values in the oxidation of phenol and epoxidation of cyclohexene. The supported HPPn Schiff base complexes of metal ions showed higher turnover number than unsupported Schiff base complexes of metal ions.

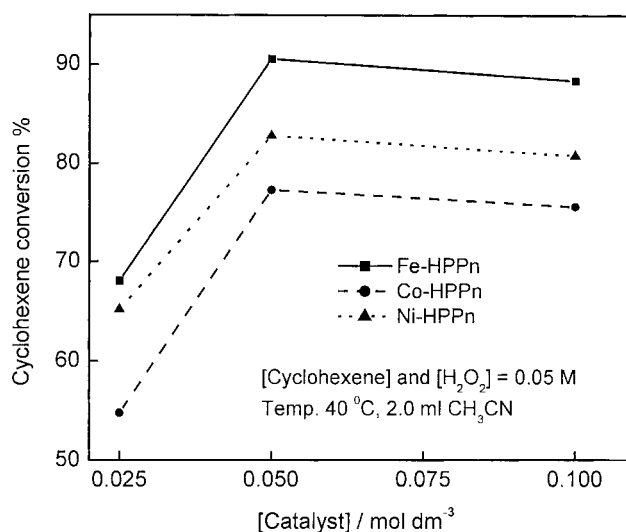
#### Effect of the catalyst concentration on oxidation and epoxidation

The oxidation of phenol and epoxidation of cyclohexene were also evaluated at different molar ratios of polymer-supported HPPn Schiff base complexes of metal ions at a constant molar ratio (1 : 1) of the substrate and oxidant.

The molar ratio of HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions was varied from 0.5 to 2.0 at a constant molarity (0.05M) of phenol/cyclohexene and  $H_2O_2$  in the reaction mixture. The conversion (%) of phenol/cyclohexene increased when the molar ratio of the catalyst was increased from 0.5 to 1.0 in the reaction mixture. The HPPn Schiff base complexes of iron(III) ions showed 73.0 and 90.6 wt % conversions of phenol and cyclohexene at a 1 : 1 : 1 molar ratio of the catalyst,  $H_2O_2$ , and phenol/cyclohexene (Figs. 9 and 10).



**Figure 9** Effect of the supported catalyst concentration on the oxidation of phenol (Ph)  $\{[Ph]/[H_2O_2] = 1 : 1 (0.05M)$  and temperature = 70°C}.



**Figure 10** Effect of the supported catalyst concentration on the epoxidation of cyclohexene (CH)  $\{[CH]/[H_2O_2] = 1 : 1 (0.05M)$  and temperature = 40°C}.

The catalytic activity of HPPn Schiff base complexes of cobalt(II) and nickel(II) ions in the conversion (%) of phenol/cyclohexene was also found to be maximum at a 1 : 1 : 1 molar ratio of the catalyst,  $H_2O_2$ , and phenol/cyclohexene (Figs. 9 and 10). When the molar ratio of Schiff base complexes of metal ions was further increased ( $>1$ ) in the reaction mixture, the conversion (%) of phenol/cyclohexene was decreased (Figs. 9 and 10), and this was attributed to the decrease in the molar ratio of phenol/cyclohexene ( $<1$ ) with respect to the molar ratio of the catalyst. The decrease in the molar ratio of phenol/cyclohexene at a high molar ratio of the catalyst reduced the concentration of the reaction intermediates (Scheme 4), which produced reaction products by a slow and rate-determining step of decomposition (steps 4a and 4b, Scheme 4). The low conversion (%) of phenol/cyclohexene at a 0.05 molar ratio of catalysts was due to an insufficient amount of the catalysts in the reaction mixture in comparison with phenol/cyclohexene and  $H_2O_2$  (Figs. 9 and 10), which reduced the formation of active species and reaction intermediates to form the reaction products (Scheme 4). The variation in the molar ratio of the catalyst showed a significant effect on the selectivity for CTL in the oxidation of phenol and selectivity of ECH in the epoxidation of cyclohexene (Table VII). The selectivity for CTL was increased from 89.8 to 93.1 wt % and the selectivity for ECH was increased from 94.6 to 98.3 wt % with the molar ratio of HPPn Schiff base complexes of iron(III) ions increasing from 0.5 to 1.0 in the reaction mixture (Table VII). With a further increase in the molar ratio of the iron(III) ion complex ( $>1$ ), the selectivity for CTL and ECH was decreased to 91.8 and 96.9 wt %, respectively. Although the variation in the molar ra-

**TABLE VII**  
Effect of the Catalyst Concentration on the Selectivity for CTL and ECH

Molarity of the catalyst (M)	Selectivity for CTL (wt %)	Selectivity for ECH (wt %)
P-HPPn-Fe		
0.025	89.8	94.6
0.050	93.1	98.3
0.100	91.8	96.9
P-HPPn-Co		
0.025	88.1	92.8
0.050	91.5	96.0
0.100	89.6	95.2
P-HPPn-Ni		
0.025	89.0	93.6
0.050	92.9	97.7
0.100	91.7	96.8

$[H_2O_2]/[Ph]/[CH] = 0.05M$ ; time = 1440 min; temperature = 70 (Ph) or 40°C (CH);  $CH_3CN = 2.0$  mL.

tio of HPPn Schiff base complexes of cobalt(II) and nickel(II) ions showed a similar trend for the selectivity of CTL and ECH, the amount of CTL and ECH was lower than that found with HPPn Schiff base complexes of iron(III) ions (Table VII). The decreasing trend in the selectivity for CTL and ECH at a high molar ratio of the catalysts (>1) was also attributed to the variations in the microenvironment<sup>20</sup> on active sites of polymer-supported catalysts. The molecular interactions in the reaction intermediates with phenol/cyclohexene were influenced significantly by the variation of the molar ratio of the catalyst in the reaction mixture; hence, the conversion (%) of phenol/cyclohexene and selectivity for CTL/ECH varied with the molar ratio of the HPPn Schiff base complexes of metal ions in the reaction mixture (Table VII). During the molar ratio variation of  $H_2O_2$  and phenol/cyclohexene, the selectivity for CTL and ECH was constant (Table IV), and from this it was clear that the interactions of the substrates in reaction intermediates (Scheme 4) depended on the amount of the catalyst used in the reaction mixture. However, these interactions in the intermediates at a high molar ratio of the catalyst (>1) affected adversely the conversion (%) of phenol/cyclohexene (Figs. 9 and 10) and selectivity for CTL/ECH.

The rate of oxidation of phenol and epoxidation of cyclohexene with supported HPPn Schiff base complexes of iron(III) ions was  $2.54 \times 10^{-6}$  and  $3.15 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ , respectively, but the rate of oxidation of phenol and epoxidation of cyclohexene with unsupported HPPn Schiff base complexes of iron(III) ions was  $2.22 \times 10^{-6}$  and  $2.89 \times 10^{-6} \text{ M L}^{-1} \text{ s}^{-1}$ , respectively, and this clearly indicated that the activity of catalysts on the polymer support was greater than that of the unsupported catalysts (Tables V and VI). The rate of oxidation of phenol and epoxidation

of cyclohexene was lower with supported HPPn Schiff base complexes of cobalt(II) and nickel(II) ions in comparison with HPPn Schiff base complexes of iron(III) ions. TON for the oxidation of phenol and epoxidation of cyclohexene was also influenced by the molar ratio of the catalyst and was highest at a 1:1:1 molar ratio of the catalyst, substrate, and oxidant in the reaction mixture. The TON value for the oxidation of phenol and epoxidation of cyclohexene was higher for unsupported and supported HPPn Schiff base complexes of iron(III) ions than for HPPn Schiff base complexes of cobalt(II) and nickel(II) ions (Tables V and VI).

#### Effect of the reaction temperature on oxidation and epoxidation

The energy of activation is useful for predicting the state and interactions of catalysts with the reactants; hence, studies were carried out at different temperatures to determine the energy of activation for the conversion of phenol and cyclohexene in the presence of unsupported and polymer-supported HPPn Schiff base complexes of metal ions. The oxidation of phenol was studied from 60 to 80°C, and the epoxidation of cyclohexene was studied with the reaction temperature varied from 30 to 50°C at a 1 : 1 : 1 molar ratio (0.05M) of phenol/cyclohexane, catalyst, and  $H_2O_2$  in the reaction mixture. The  $k$  values for these reactions were determined at different temperatures and were used to calculate the energy of activation. The oxidation of phenol showed an increasing trend with the reaction temperature increasing from 60 to 70°C, but the epoxidation of cyclohexene was increased with the reaction temperature increasing from 30 to 40°C (Table VIII).

With further increases in the reaction temperature beyond 70 and 40°C, the conversion of phenol and cyclohexene showed a decreasing trend with unsupported and polymer-supported HPPn Schiff base complexes of metal ions (Table VIII).

The decrease in the oxidation of phenol and epoxidation of cyclohexene at a high temperature was due to the decomposition of  $H_2O_2$  without oxidation of the phenol and cyclohexene. The decomposition of  $H_2O_2$  at a high temperature reduced the amount of active species (Scheme 4) in the reaction mixture; hence, the conversion of phenol and cyclohexene decreased. The increase in the reaction temperature beyond 70 and 40°C reduced the selectivity of CTL and ECH, and a similar trend was shown by unsupported HPPn Schiff base complexes of metal ions (Table VIII). The variation in selectivity for CTL and ECH with the reaction temperature was due to the variation in the microenvironment<sup>20</sup> in the reaction intermediate, which influenced the reactant-catalyst interactions and intramolecular electron-transfer pro-

**TABLE VIII**  
**Effect of the Reaction Temperature on the Conversion of Phenol (Ph)/Cyclohexene (CH) and Product Selectivity**

Temperature (°C)	P-HPPn-Fe		P-HPPn-Co		P-HPPn-Ni	
	Ph conversion (wt %)	CTL selectivity (wt %)	Ph conversion (wt %)	CTL selectivity (wt %)	Ph conversion (wt %)	CTL selectivity (wt %)
60	46.6	89.1	38.0	86.8	41.4	87.1
70	73.0	93.1	59.0	91.5	65.0	91.9
80	66.5	90.8	49.2	88.9	58.2	90.0
	CH conversion (wt %)	ECH selectivity (%)	CH conversion (wt %)	ECH selectivity (%)	CH conversion (wt %)	ECH selectivity (%)
30	75.3	94.3	64.9	87.4	72.3	84.7
40	90.6	98.1	77.3	92.8	82.8	89.9
50	85.3	96.5	74.9	89.9	80.9	86.2

$[\text{H}_2\text{O}_2]/[\text{Catalyst}]/[\text{Ph}] = 0.05\text{M}$ ; time = 1440 min;  $\text{CH}_3\text{CN} = 2.0\text{ mL}$ .

cess in the reaction intermediate before its decomposition to form reaction products. The nature of the interactions and electron-transfer process in the intermediate were responsible for controlling the product selectivity in the reaction. At high temperatures, the interactions of the reactants and catalyst in the intermediates were affected adversely; hence, the selectivity for CTL and ECH was reduced (Table VIII). The values of  $k$  for the conversion of phenol and cyclohexene were  $5.05 \times 10^{-5}\text{ s}^{-1}$  and  $6.29 \times 10^{-5}\text{ s}^{-1}$ , respectively, with polymer-supported HPPn Schiff base complexes of iron(III) ions, but the value of  $k$  was lower with HPPn Schiff base complexes of cobalt(II) and nickel(II) ions. The increase in the value of  $k$  in the conversion of phenol and cyclohexene with the reaction temperature was an indication that the oxidation of phenol and epoxidation of cyclohexene were energy-activated processes and that supported catalysts played a significant role in decreasing the energy of activation for the conversion of phenol and cyclohexene. The activation energy for the conversion of phenol and cyclohexene with polymer-supported Schiff base complexes of iron(III) ions was 12.7 and 10.0 kJ/mol, respectively, but it was higher with HPPn Schiff base complexes of cobalt(II) and nickel(II) ions (Tables V and VI). The activation energy for these reactions with unsupported HPPn Schiff base complexes of metal ions was more than that for these reactions with polymer-supported HPPn Schiff base complexes of metal ions. The polymer support played a significant role in reducing the energy of activation for the electron-transfer process in the reaction intermediate;<sup>20,50</sup> hence, the activation energy for the conversion (%) of phenol and cyclohexene was lower with polymer-supported Schiff base complexes of metal ions than with unsupported metal-ion complexes. The variation in the energy of activation with HPPn Schiff base complexes of iron(III), cobalt(II), and nickel(II) ions was due to the differences in their structures and the electronic configurations of metal ions in the

complexes, which ultimately controlled the conversion (%) and product selectivity (Scheme 4).

## CONCLUSIONS

Polymer-supported metal-ion complexes of the HPPn Schiff base were synthesized and characterized for their structures and catalytic activity in the oxidation of phenol and epoxidation of cyclohexene. The polymer-supported HPPn Schiff base complexes of metal ions showed higher catalytic activity than the unsupported metal-ion complexes. The Schiff base complexes of iron(III) ions were more catalytic in the conversion of phenol and cyclohexene than complexes of cobalt(II) and nickel(II) ions. Phenol was selectively oxidized to CTL and cyclohexene was selectively oxidized to ECH with unsupported and supported HPPn Schiff base complexes of metal ions in the presence of  $\text{H}_2\text{O}_2$  as an oxidant. The supported catalysts showed a significant decrease in the energy of activation for the oxidation of phenol and epoxidation of cyclohexene in comparison with the unsupported catalysts, and this clearly suggested that the polymer support was able to improve the catalytic activity of Schiff base complexes of metal ions; the supported catalysts were reusable up to six recyclings without any loss in their activity.

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