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Article

Novel polystyrene-anchored zinc complex: Efficient catalyst for phenol oxidation

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ABSTRACT

The novel recyclable free –ONNO- tetradentate Schiff base ligand N,N′-bis(2-hydroxy-3-methoxybenzaldehyde)4-methylbenzene-1,2-diamine (3-MOBdMBn) was synthesized. Complexation of this ligand with zinc (3-MOBdMBn-Zn) was performed, and the catalytic activity of the complex was evaluated. The polymer-supported analog of this complex (P-3-MOBdMBn-Zn) was synthesized, and its catalytic activity was studied. These free and polymer-anchored zinc complexes were prepared by the reactions of metal solutions with one molar equivalent of unsupported 3-MOBdMBn or P-3-MOBdMBn in methanol under nitrogen. The catalytic activity of 3-MOBdMBn-Zn and P-3-MOBdMBn-Zn was evaluated in phenol oxidation. The activity of P-3-MOBdMBn-Zn was significantly affected by the polymer support, and the rate of phenol conversion was around 50% for polystyrene-supported 3-MOBdMBn. The experimental results indicated that the reaction rate was affected by the polymer support, and the rate of phenol conversion was 1.64 μmol/(L·s) in the presence of polystyrene-supported 3-MOBdMBn.

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1. Introduction

Schiff base complexes have various applications in organic reactions such as oxidation [1,2], olefin epoxidation [3,4], and polymerization of ethenones to give narrow molecular-mass distributions [5,6]. However, homogeneous Schiff base catalytic systems have two major disadvantages: (1) lack of product control, which causes reactor fouling and (2) limited use in solution processes. The binding of Schiff base metal catalysts to polymer supports is a promising solution to these problems. In general, the catalytic activity of heterogeneous Schiff base systems (or supported systems) is lower than that of the homogeneous analogs, but polymer-supported transition-metal complexes have shown high catalytic activity [7,8] compared with homogeneous and unsupported catalysts. Polymer-supported palladium complexes have been used in Heck reactions [9–11], generating the corresponding products in good to excellent yields. Heterogeneous catalysts are particularly attractive for phenol oxidation because of their practical advantages and catalyst reusability. The Schiff base complexes of metal ions have also been used in phenol oxidation [12,13].

Phenol oxidation is an industrially important reaction because its products, i.e., catechol and hydroquinone, have a range of applications as antioxidants, polymerization inhibitors, photographic chemicals, flavoring agents, and drug intermediates. Since 1970, phenol oxidation has been widely investigated using various homogeneous and heterogeneous catalysts [13]. Phenol is an intermediate in the oxidation of many
aromatic compounds, and it is toxic and resistant to biotreatment. The treatment of wastewater containing highly concentrated, toxic, or poorly biodegradable compounds by oxidation of the organic pollutants to non-toxic products in the presence of a catalyst is a promising approach [14,15].

The oxidation of phenols using various chemical reagents such as H2O2, permanganate, molecular oxygen, and ozone is widely used [16]. The use of H2O2 has the advantage of producing oxygen, which can be used to augment biological degradation [17]. The use of H2O2 as an alternative to current industrial oxidation processes has environmental advantages such as (1) replacement of stoichiometric metal oxidants, (2) replacement of halogens, (3) replacement or reduction of solvent use, and (4) avoidance of salt by-products. H2O2 works as an alternative to current industrial oxidation processes has environmental advantages such as (1) replacement of stoichiometric metal oxidants, (2) replacement of halogens, (3) replacement or reduction of solvent use, and (4) avoidance of salt by-products. H2O2 works efficiently with H2O2 [18]. In the present investigation, phenol oxidation was chosen as the model reaction to study the catalytic activity of the unsynthesized unsupported and polymer-supported zinc metal complexes; zinc was used because it is a bioactive metal.

Although the oxidation of phenol in the presence of polymer-supported Schiff base transition-metal complexes has been reported [8], the catalytic activity of the zinc complex of the Schiff base \(N,N'-\text{bis(2-hydroxy-3-methoxybenzaldehyde)4-methylbenzene-1,2-diamine} (\text{3-MOBdMBn})\) has not been reported in the literature. We therefore attempted to synthesize and characterize polystyrene-supported transition-metal complexes of 3-MOBdMBn, evaluate their catalytic activity in phenol oxidation with H2O2 as the oxidant, and compare their activity with that of the unsupported zinc complex.

2. Experimental

2.1. Materials

Divinylbenzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai, India. Anhydrous zinc chloride was purchased from Thermo Fisher Scientific India Pvt., Ltd., Mumbai, India and used without further purifications. Phenol, H2O2 (30.0 wt%), 2-hydroxy-3-methoxybenzaldehyde (3-MOBd), and 4-methylbenzene-1,2-diamine (MBn) were procured from E. Merck, India. Other chemicals and solvents were of analytical grade (> 99.0 wt%) and used after drying.

2.2. Synthesis of 3-MOBdMBn Schiff base and its zinc complex

The 3-MOBdMBn Schiff base was synthesized using a modified version of the procedure reported in the literature [7]. A reaction mixture consisting of 3-MOBd (20.00 mmol, 3.04 g) and MBn (10.00 mmol, 1.22 g) in methanol was refluxed at 60 °C for 2 h. The reaction mixture was cooled to a low temperature, producing light-straw-colored crystals, which were filtered and recrystallized with methanol. The metal complex of 3-MOBdMBn was prepared by refluxing a methanolic solution (100 mL) of Schiff base (20.00 mmol, 7.81 g) and zinc salt (20.00 mmol, 2.725 g) in a round-bottomed flask at 60 °C for 6 h. All reactions were performed under nitrogen. The metal complex was recrystallized from dichloromethane and dried in a vacuum desiccator.

2.3. Synthesis of P-3-MOBdMBn Schiff base and its zinc complex

Polymer-anchored zinc complexes were prepared by nitrosation of 3-MOBdMBn (7.81 g, 20.00 mmol) with sodium nitrite (20.00 mmol) in 1.0 mol/L hydrochloric acid (100 mL) in an ice bath. The resultant NO-3-MOBdMBn was filtered and washed with hot and cold water to remove reaction impurities. Reduction of NO-3-MOBdMBn was performed using the nitrosated Schiff base (20.00 mol) in 1.0 mol/L hydrochloric acid (50 mL) in the presence of metallic iron, which produced \(\text{H}_2\text{N',N'-bis(4-amino-2-hydroxy-3-methoxybenzaldehyde)-4-methylbenzene-1,2-diamine (A-3-MOBdMBn)}\). Then methanol-swollen cross-linked chloromethylated polystyrene beads (5.0 g) were refluxed in methanol (50 mL) containing A-3-MOBdMBn (20 mmol). After 10 h, the polymer beads with anchored 3-MOBdMBn were separated and dried in a vacuum desiccator. Zinc ions were then loaded by keeping P-3-MOBdMBn (5.0 g) for 10 h in 50 mL of an aqueous solution of zinc ions. The metal ion loadings on the free and polymer-supported 3-MOBdMBn were calculated as a complexation of the metal ions based on the initial amount of 3-MOBdMBn and the amount of metal ions loaded on the polymer beads.

2.4. Characterization of the samples

Infrared (IR) spectra (KBr pellets) were recorded using a Perkin-Elmer 1600 Fourier-transform (FT) IR spectrophotometer. Electronic spectra were recorded with a Shimadzu 1601 PC ultraviolet-visible (UV-Vis) spectrophotometer using sample mulls in a cuvette. Thermogravimetric (TG) analysis was performed using a Perkin-Elmer Pyris Diamond thermal analyzer under nitrogen at a heating rate of 10 °C/min. The metal ion loading on the Schiff base was determined by analyzing the loading solution using a Perkin-Elmer 3100 atomic absorption spectrometer at the zinc ion \(\lambda_{\text{max}}\). The compositions of 3-MOBdMBn and its zinc complex were estimated using a Haraeus Carlo Ebra 1108 elemental analyzer. 1H nuclear magnetic resonance (NMR) spectra were recorded with a Bruker FT-NMR 300 MHz spectrometer using DMSO-\(d_6\) as the solvent and tetramethylsilane as an internal reference. The magnetic moments (\(\mu\)) of the metal complexes were measured using a Vibrating Sample Magnetometer-155. The molecular mass of 3-MOBdMBn and its zinc complex was determined using a vapor pressure osmometer (Merck VAPRO 5600, Germany).

2.5. Catalytic activity of zinc complexes in phenol oxidation

Phenol oxidation was performed using H2O2 as the oxidant, with a fixed ionic strength (0.10 mol/L) and hydrogen ion concentration (\(pH = 7.0\)) in the reaction mixture. A calculated amount of polymer-anchored zinc was placed in a two-necked round-bottomed flask containing phenol (4.70 g, 0.05 mol/L);
H₂O₂ (5.67 g, 30.0 wt%, 0.05 mol/L) was added to the reaction mixture with acetonitrile (2 mL) as an internal standard in a nitrogen atmosphere. The phenol conversion was determined by removing aliquots of the reaction mixture at different time intervals and analyzing them using gas chromatography. The reaction products were identified based on the retention time of standards, and the peak areas in the chromatograms were used to measure product selectivity. Phenol, catechol, and 4-hydroquinone were determined using a fused-silica capillary column (XE-60; 30 m × 0.2 mm × 0.3 mm; Perkin-Elmer Corp., Norwalk, CT, USA). The temperatures of the injection port and column were the same as those in the reactions, and the carrier gas was supplied at a rate of 20.0 mL/min.

3. Results and discussion

3.1. TG analysis

The thermal stability of the unsupported and supported catalysts was determined to assess their applicability in high-temperature reactions and to confirm the complexation of metal ions with the polymer-anchored Schiff base. Thermogravimetric analysis of the polymer-supported 3-MOBdMBn (P-3-MOBdMBn) showed a mass loss of 39.1% at 500 °C, but the zircon(II) ion complex showed a mass loss of 27.0% at the same temperature, clearly indicating that the zircon ion complex was more stable [19] than the ligand (Fig. 1). The free and polymer-supported metal complexes of 3-MOBdMBn were also characterized using IR and UV techniques to confirm complexation of metal ions, and the structure and geometry of the metal complexes were determined on the basis of elemental analysis and the magnetic properties of the metal complexes.

3.2. Characterization of 3-MOBDMBn Schiff base

The 3-MOBDMBn Schiff base was produced in substantial yield (91.6 wt%) by refluxing 3-MOBd and MBn (Scheme 1). The IR spectrum (Fig. 2(1)) of 3-MOBDMBn showed absorption bands at 1609 (C=N), 1263 (C–O, phenolic), and a broad band between 3200 and 2910 cm⁻¹, which was assigned to phenolic OH. Elemental analysis of 3-MOBDMBn (wt%): C 70.75, N 7.17, and H 5.68; calcld (%): C 69.82, N 7.03, and H 6.31, corresponding to C₂₃H₂₂N₂O₄, the empirical formula of 3-MOBDMBn [7,12].

The molecular mass of the Schiff base was 390.43 g/mol (calcld 389.37 g/mol). The electronic spectrum of 3-MOBDMBn (Fig. 3) showed absorption bands at 289 and 347 nm, which were assigned to π → π* and n → π* transitions, respectively. The 1H-NMR spectrum of the Schiff base showed signals at δ = 3.71 (6H), 2.79 (3H), 5.13 (2H), 6.60 (2H), 6.98 (2H), 7.35 (3H), 7.41 (2H), and 8.61 (2H), corresponding to the structure of 3-MOBDMBn.

3.3. Synthesis and characterization of A-3-MOBDMBn Schiff base and its anchoring on polymer beads

The nitrosoation of 3-MOBDMBn was carried out in the presence of NaN₃/HCl, producing NO-3-MOBDMBn in 84.5% yield (Scheme 2); elemental analysis (%): C 61.60, N 12.49, and H 4.50; calcld (%): C 62.01, N 12.17, and H 4.95, corresponding to C₂₃H₂₀N₄O₈, the formula of the nitrosated Schiff base. The molecular mass of NO-3-MOBDMBn was 448.43 g/mol (calcld 447.02 g/mol). The IR spectrum of NO-3-MOBDMBn showed

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**Scheme 1.** Synthesis of N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)-4-methylbenzene-1,2-diamine Schiff base (3-MOBdMBn).
absorption bands at 1604 (C=N), 1260 (C–O, phenolic), and 1500 and 1315 cm\(^{-1}\) for the N–O group. The NMR signals of NO-3-MOBdMBn shifted compared with those of pure 3-MOBdMBn. The NO-3-MOBdMBn had proton signals at \(\delta = 3.75\) (6H), 2.82 (3H), 5.15 (2H), 7.15 (2H), 7.36 (3H), 7.66 (2H), and 8.64 (2H), corresponding to the structure of NO-3-MOBdMBn. The protons ortho to the nitroso group in 3-MOBdMBn were deshielded, therefore their signals appeared at \(\delta = 7.15\) and 7.66 instead of \(\delta = 6.60\) and 6.98, respectively, for pure 3-MOBdMBn. The proton signal at \(\delta = 6.91\) was missing because of substitution of the nitroso group in the benzene ring. NO-3-MOBdMBn was reduced with iron(II) ions in the presence of hydrochloric acid, providing A-3-MOBdMBn in 87.3 wt\% yield; elemental analysis (%): C 65.70, N 13.33, and H 5.75; calcld (%): C 63.92, N 13.21, and H 7.02, corresponding to \(C_{23}H_{24}N_4O_3\), the empirical formula of the Schiff base. The molecular mass of A-3-MOBdMBn was 420.46 g/mol (calcld 418.23 g/mol). The IR spectrum of A-3-MOBdMBn had absorption bands at 1600 (C=N), 1255 (C–O, phenolic), and a band between 1627 and 1616 cm\(^{-1}\) for the C–N group. The \(^1\)H-NMR spectrum of A-3-MOBdMBn showed proton signals at \(\delta = 3.72\) (6H), 2.81 (3H), 4.15 (4H), 5.15 (2H), 6.16 (2H), 7.36 (3H), 6.46 (2H), and 8.63 (2H), corresponding to the structure of A-3-MOBdMBn, shown in Scheme 2. A new proton signal from the amino group appeared at 4.15 (4H).

The synthesized Schiff base was anchored on cross-linked chloromethylated polystyrene beads by refluxing A-3-MOBdMBn with polymer beads in dimethylformamide at 60 °C for 8 h. The amount of A-3-MOBdMBn anchored on the polymer beads was 86.0 wt\% (Scheme 3). Anchoring of A-3-MOBdMBn on the polymer beads was confirmed by comparing the IR spectrum of 3-MOBdMBn anchored on polymer beads with that of pure polymer beads. The IR spectrum of the polymer-anchored Schiff base showed absorption bands at 1594 (C=N) and 1246 cm\(^{-1}\) (C–O, phenolic), which were absent in the IR spectrum of the pure polymer beads but present in the free Schiff base. The IR spectrum of the pure polymer beads showed an absorption band at 1262 cm\(^{-1}\), attributed to the chloromethyl C–Cl bond in the cross-linked polymer beads [7]. The decrease in the intensity of the absorption band at 1262 cm\(^{-1}\) for the polymer-anchored 3-MOBdMBn compared with that for the pure polymer beads was evidence of anchoring of 3-MOBdMBn on the polymer beads (Fig. 2(2)). The appearance of new absorption bands and shifts in the characteristic absorption bands of 3-MOBdMBn also confirmed anchoring of 3-MOBdMBn on the polymer beads.

3.4. Characterization of free and polymer-anchored zinc complexes of 3-MOBdMBn Schiff base

Zinc ions were complexed with free and polymer-supported 3-MOBdMBn by refluxing the free Schiff base (Scheme 4) and polymer-anchored Schiff base in solutions of a metal salt at 60 °C for 10 h (Scheme 5). The metal complexes 3-MOBdMBn-Zn and P-3-MOBdMBn-Zn were separated and purified, and then their structures and the amounts of metal ions were determined. The amounts of zinc(II) ions complexed with free 3-MOBdMBn and the polymer-anchored Schiff base were 74.56 wt\% and 78.24 wt\%, respectively.
The complexation of metal ions with 3-MOBdMBn resulted in significant changes in the IR bands of the C=N and C−O groups, and new absorption bands appeared as a result of the formation of M−O and M−N bonds in the metal complexes. The disappearance of the phenolic absorption band between 2910 and 3200 cm\(^{-1}\) in the IR spectrum of 3-MOBdMBn after complexation with metal ions was evidence for complexation of metal ions with 3-MOBdMBn. On complexation with zinc(II) ions, the C=N absorption band of the free Schiff base shifted from 1609 to 1591 cm\(^{-1}\), and that of the polymer-supported Schiff shifted from 1594 to 1575 cm\(^{-1}\) (Fig. 4) [7].

Complexation with zinc(II) ions resulted in a new absorption band at 403 cm\(^{-1}\) for the free Schiff base and at 401 cm\(^{-1}\) for the polymer-anchored Schiff base, as a result of formation of M−N bonds between zinc(II) ions and the Schiff base. Metal ion complexation also led to new bands as a result of formation of bonds between metal ions and phenolic oxygen (−O−M; Table 1). The complexation of metal ions with the Schiff base was further confirmed by comparing the electronic spectra of metal-complexed and pure 3-MOBdMBn. The complexation of zinc(II) ions with 3-MOBdMBn resulted in a hypochromic shift of the π → π\(^*\) transition from 289 to 265 nm, and of the n → π\(^*\) transition from 347 to 307 nm; similar shifts were seen for the polymer-supported catalyst (Table 1). These electronic transitions correspond to the t\(_{2g}^6\) e\(_g^4\) configurations of the zinc(II) ions in these complexes. The magnetic moment (\(\mu\)) of the Schiff base complexes with zinc(II) ions was 0.71 BM, indicating a diamagnetic and tetrahedral structure with sp\(^3\) hybridization.

### 3.5. Phenol oxidation

The catalytic activity of the free and polymer-supported 3-MOBdMBn-Zn was evaluated by studying the phenol oxidation in the presence of H\(_2\)O\(_2\). Gas chromatography was used to determine the product selectivity and estimate the percentage conversion of phenol. Catechol was the major reaction product in the oxidation of phenol (Scheme 6). The formation of the reaction products was attributed to catalytic behavior of the metal complexes of 3-MOBdMBn.

These investigations also confirmed that the type of polymer support plays an important role in controlling the catalytic activity. In addition, stable active sites on the polymer support prevent deactivation of the catalyst on repeated use [9]. The anchoring of active species minimizes poisoning by impurities and improves the efficiency of active species by reducing their dimerization and aggregation, as observed under homogeneous conditions. The activity of the catalyst depends on the properties of the support; polymeric supports give better results [20] because of the flexibility of the polymer backbone [21,22], and because of their compatibility with reaction media. The anchoring of catalysts on polymer supports improves the loading of metal ions and controls the interactions between catalysts and substrates; it also enhances the activity and selectivity of the catalysts [23,24]. A polymer support prevents the aggrega-

![Scheme 4. Complexation of zinc ions with free 3-MOBdMBn.](image)

![Scheme 5. Loading of zinc ions on polymer-supported Schiff base (P-3-MOBdMBn-Zn).](image)

![Table 1](image)

![Fig. 4. FTIR spectrum of P-3-MOBdMBn-Zn complex.](image)

![Scheme 6. Phenol oxidation.](image)
tion of active sites and increases the activity of the catalyst. Supported catalysts are more thermally stable than their unsupported analogs [19] as shown in Fig. 1.

The polymer support facilitated decomposition of intermediates, therefore the percentage conversion of phenol was higher with the polymer-supported metal complex than with the free metal complex of 3-MOBdMBn (Fig. 5). The conversion of phenol with the unsupported catalyst was high at 240 min and then became almost constant because of a substantial decrease in the concentration of oxidant and substrate in the reaction mixture. Similar trends in substrate conversion were observed with the supported catalyst at different time intervals.

The amount of phenol oxidized by H₂O₂ was almost equal to the sum of the amounts of catechol and hydroquinone produced, which indicates that almost no other reaction products such as polymeric phenols were formed. However, the reaction showed high selectivity for catechol, as determined from the areas of the gas chromatogram peaks. The supported catalyst was recycled, and its catalytic activity was evaluated. The efficiency of the supported catalyst remained almost constant up to six cycles and then decreased significantly (Table 2), possibly because of decomposition of the catalyst in the reaction medium or catalyst extraction into the organic solvent during product isolation [25]. The product selectivity for catechol was unaffected by using a recycled catalyst, indicating structural stability of the metal complex on the polymer support; this was confirmed by comparing the IR spectra of the recycled and freshly prepared catalysts.

The rate of phenol conversion was high (1.64 μmol/(L·s)) in the presence of the P-3-MOBdMBn-Zn and low (0.86 μmol/(L·s)) in the presence of the unsupported analog (Table 3); a similar trend was observed for the turnover number (TON) at H₂O₂:phenol:catalyst molar ratio = 1:1:1.

3.6. Effect of H₂O₂, phenol, and catalyst concentrations on phenol oxidation

The oxidation of phenol was studied using different molar ratios of H₂O₂ to phenol, from 0.5 to 2.0, at constant molarities of the substrate and catalyst (0.05 mol/L), in acetonitrile (2.0 mL) at 70 °C. When the molar ratio of H₂O₂ was changed from 0.5 to 1.0, phenol oxidation increased in the presence of P-3-MOBdMBn-Zn (Fig. 6). However, when the molar ratio of H₂O₂ was further increased (>1), the phenol oxidation decreased; a similar trend was observed for the unsupported 3-MOBdMBn-Zn analog. The decreased phenol conversion was caused by the decrease in the molar ratios of phenol and the catalyst with respect to that of H₂O₂.

The catalytic efficiency of 3-MOBdMBn-Zn in phenol oxidation was evaluated at different molar ratios of phenol in the reaction mixture, with the molar ratio of H₂O₂ to the catalyst being kept constant. The molar ratio of phenol was changed from 0.5 to 2.0 with respect to the molar ratio of H₂O₂ to the catalyst. The concentrations of H₂O₂ and the catalyst were kept constant (0.05 mol/L). When the molar ratio of phenol was increased from 0.5 to 1.0, the conversion of phenol increased significantly over the P-3-MOBdMBn-Zn (Fig. 6), but when the molar ratio of phenol was increased further (>1), the conversion of phenol decreased; this was because of the significant decrease in the molar ratio of H₂O₂ to the catalyst in the reaction mixture.

Table 3
Phenol conversion, selectivity for catechol, and kinetic parameters of phenol oxidation over 3-MHBdMBn-Zn and P-3-MOBdMBn-Zn.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>TON [g/(mol·h)]</th>
<th>Rate [μmol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-MOBdMBn-Zn</td>
<td>25.9</td>
<td>89.4</td>
<td>5.83</td>
<td>0.86</td>
</tr>
<tr>
<td>P-3-MOBdMBn-Zn</td>
<td>48.7</td>
<td>90.0</td>
<td>11.14</td>
<td>1.64</td>
</tr>
</tbody>
</table>

[Phenol] = [Catalyst] = [H₂O₂] = 0.05 mol/L, 70 °C, CH₃CN = 2.0 mL.

Fig. 5. Effects of reaction time on phenol oxidation in the presence of P-3-MOBdMBn-Zn and 3-MOBdMBn-Zn. [Phenol] = [Catalyst] = [Oxidant] = 0.05 mol/L, 70 °C.

Fig. 6. Effect of H₂O₂, phenol, and catalyst concentrations on phenol oxidation in the presence of P-3-MOBdMBn-Zn at 70 °C.

Table 2
Recycling of P-3-MOBdMBn-Zn in phenol oxidation.

<table>
<thead>
<tr>
<th>Recycle number</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>48.7</td>
<td>90.0</td>
</tr>
<tr>
<td>2</td>
<td>47.3</td>
<td>90.3</td>
</tr>
<tr>
<td>4</td>
<td>45.2</td>
<td>88.6</td>
</tr>
<tr>
<td>6</td>
<td>41.2</td>
<td>84.2</td>
</tr>
<tr>
<td>8</td>
<td>24.4</td>
<td>81.7</td>
</tr>
</tbody>
</table>

[Phenol] = [Catalyst] = [H₂O₂] = 0.05 mol/L, 70 °C, CH₃CN = 2.0 mL.
tion mixture compared with the molar ratio of phenol. The oxidation of phenol was also evaluated at different molar ratios of P-3-MOBdMBn-Zn at a constant molar ratio (1:1) of the substrate and oxidant. The molar ratio of the Schiff base complex with zinc(II) ions was changed from 0.5 to 2.0 at constant molarities (0.05 mol/L) of phenol and H$_2$O$_2$ in the reaction mixture. The conversion of phenol showed the same trend as the changes in substrate concentration.

### 3.7. Mechanism of phenol oxidation

Based on the experimental results for the oxidation of phenol over free and supported 3-MOBdMBn-Zn, the following reaction steps are proposed (Scheme 7). The free and polymer-supported 3-MOBdMBn-Zn produced active species, Zn-3-MOBdMBn-HOO$^-$, through fast interactions with H$_2$O$_2$ and 3-MOBdMBn. The active species were then involved in the formation of intermediates, Zn-3-MOBdMBn-Ph-HOO$^-$, through interactions with phenol in a rapid equilibrium ($K$). The intermediate Zn-3-MOBdMBn-Ph-HOO$^-$ facilitated nucleophilic attack of -OOH species on the ortho and para positions of phenol, producing hydroxy-substituted phenols. The reaction products, catalyst, and hydroxyl ions were formed through decomposition of the intermediates; finally, the hydroxyl ions reacted with hydrogen ions, which were produced in the initial step.

### 4. Conclusions

Unsupported and polymer-supported zinc complexes of 3-MOBdMBn were synthesized, and their structure and catalytic activity in phenol oxidation were determined. The catalytic activity of P-3-MOBdMBn-Zn was higher than that of the free analog. The phenol oxidation showed high selectivity for catechol. The oxidation rate and TON of the supported catalyst were higher than those of the unsupported catalyst, which clearly suggested that the polymer support played a significant role in increasing the phenol oxidation rate. The effect of H$_2$O$_2$, phenol, and catalyst concentrations on phenol oxidation was important for the polymer-supported zinc complex. Phenol oxidation conversion was maximum at the phenol:H$_2$O$_2$:catalyst ratio of 1:1:1.

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标题中译文：
新的聚苯乙烯负载锌化合物: 高效苯酚氧化催化剂
Synthesis, Structural Studies and Catalytic activity of Copper(II) Complex Supported by N, N’-bis (2-Hydroxy-3-Methoxybenzaldehyde) 4-Methylbenzene-1, 2-Diamine

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Abstract

A novel robust method for synthesis of 3-MOBDMBn-Cu complex, supported by ONNO-tetradentate Schiff-base ligand is presented. This copper complex is prepared by the reactions of metal solution with one molar equivalent of 3-MOBDMBn (N, N’-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1, 2-diamine) Schiff-base ligand in methanol under nitrogen atmosphere. In contrast to other catalysts, the main advantage of this catalyst system was that the cost of the catalyst was remarkably low and it can be recycled up to eight times, due to its easily accessible materials and the simple synthetic route. The higher efficiency of complexation of copper ion on the 3-MOBDMBn Schiff base was another advantage of this catalyst system. The structural study reveals that copper(II) complex is of square planar geometry. The catalytic activity of copper complex toward the oxidation of phenol is investigated. Experimental results indicate that the rate of phenol conversion was 6.055 x 10^-6 moles dm^-3 s^-1 with turnover number 49.632 g mol^-1 Cu hr^-1 at 30 min.

Keywords: Schiff base, catalysis, organometallic catalyst, copper, phenol oxidation

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INTRODUCTION

During the past decade, Schiff base complexes of transition metals have shown versatile applications in different organic transformation reactions such as oxidation, epoxidation of olefins, polymerization of ethylenes, Heck reaction to generate the corresponding products in good to excellent yields. The Schiff base complexes of metal ions have been used in the oxidation of phenols.

On the other hand, removal of environmental pollutants such as phenol (a product of the decomposition of organic materials, liquid manure, and the atmospheric degradation of benzene) through oxidation processes receives increasing attention. The general methods of phenol removal, that include sorption over natural surfaces like activated carbon, or sorption over organophilic clay that was modified with organic polymers exist, is not always enough and thus, the phenol need to get oxidized or reduce them to less harmful products. Oxidation of phenols using various chemical reagents such as, hydrogen peroxide, permanganate, molecular oxygen and ozone, are widely used. The use of hydrogen peroxide has the advantage of producing oxygen and can be used to augment biological degradation. Hydrogen peroxide works either alone or with a catalyst. But with catalyst, it gives better results. Iron is the most common homogeneous catalyst for hydrogen peroxide.

Although the oxidation of phenol in the presence of Schiff base transition metal complexes have been reported, the catalytic activity of copper complex of the 3-MOBDMBn (N, N’-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1, 2-dianime) Schiff base was another advantage of this catalyst system. The structural study reveals that copper(II) complex is of square planar geometry. The catalytic activity of copper complex toward the oxidation of phenol is investigated.
diamine) Schiff base has not been reported in the literature. Hence, attempts have been made to synthesize and characterize copper complex of 3-MOBDMBn Schiff base and to evaluate their catalytic activity for the oxidation of phenol in the presence of H₂O₂ as an oxidant.

**EXPERIMENTAL**

**Materials**
The salt of copper (II) ion was purchased from Ranbaxy, Mumbai, India. The phenol, hydrogen peroxide (30.0 wt%), 2-hydroxy-3-methoxybenzaldehyde (3-MOBd) and 4-Methylbenzene-1, 2-diamine (MBn) were procured form E. Merck, India. Other chemicals and solvents were of analytical grade (>99.0 wt%) and solvents are used after drying.

**Characterization of the 3-MOBDMBn Schiff base and its Copper Complex**
IR spectra were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra were recorded with Shimadzu 1601 PC UV–Vis Spectrophotometer by using sample mull in a cuvette. Thermo gravimetric analysis was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10ºC min⁻¹.

The loading of metal ions on Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_max of copper ion. The ¹H NMR spectra was recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d₆ as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (µ) of metal complexes was measured using Vibrating Sample Magnetometer-155. The molecular weight of 3-MOBDMBn Schiff base and its copper complex was determined using a Vapor Pressure Osmometer (Merck VAPRO 5600, Germany).

**Synthesis of N, N'-bis (2-hydroxy-3-methoxy benzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MOBDMBn) and its Copper Complex**
3-MOBDMBn Schiff base was synthesized by the modified procedure reported in the literature [19]. The reaction mixture containing 2-hydroxy-3-methoxybenzaldehyde (20.00 mmol, 3.04 g) and 4-Methylbenzene-1,2-diamine (10.00 mmol, 1.22 g) in methanol was refluxed at 60ºC for about 2 h. The reaction mixture on cooling at low temperature produced light straw yellow colored crystals, which were filtered and recrystallized with methanol. The metal complexes of 3-MOBDMBn Schiff base were prepared taking 100 ml methanolic solution of mixture of Schiff base (20.00 mmol, 7.81 g) and 20.00 mmol of copper ion in a round bottom flask and refluxing at 60ºC for 6 h. All reactions were performed under nitrogen atmosphere. Finally, metal complexes were recrystallized in dichloromethane and dried in a vacuum desiccator. The loading of copper ion on 3-MOBDMBn Schiff base was calculated as complexation of copper ion using the amount of 3-MOBDMBn Schiff base taken initially and the amount of copper loaded, which was determined by using Atomic Absorption spectrometer.

**Catalytic Activity of Metal Complexes in Oxidation of Phenol**
The oxidation of phenol was carried out using hydrogen peroxide as the oxidant at hydrogen ions concentration (pH 7.0) in the reaction mixture. A calculated amount of copper complex was taken in a two-necked round-bottomed flask containing 50 mmol of phenol (4.70 g) and 88 mmol (5.67 g) of hydrogen peroxide (30.0 wt%) was added in the reaction mixture on cooling at low temperature. The loading of the reaction mixture was refluxed at 60ºC for about 2 h. The reaction mixture was then taken at different time intervals and analyzed with the gas chromatography instrument Hewlett –Packard 1050 model. For analysis of phenol, catechol and hydroquinone, a fused silica capillary column (XE-60, 30 m×0.2 mm×0.3 µm) was used. The temperature of injection port and column was 280 and 180°C, respectively, and carrier gas was supplied at 20 mLmin⁻¹. To identify the reaction products, the retention times of standards were used, and peak areas in the chromatograms were used to measure product selectivity.
RESULTS AND DISCUSSION
The thermal stability of the catalysts was analyzed for their applications in high-temperature reactions and to provide proof for the complexation of metal ions with Schiff base. The TGA of 3-MOBDMBn Schiff base showed a weight loss of 34.5 wt% at 500°C, but its copper(II) ion complexes showed a weight loss of 30.1 wt% at same temperature, which was clear indication that copper ion complex was more stable in comparison to ligand (Figure 1). In addition to thermal analysis, the copper complex of 3-MOBDMBn Schiff base was also characterized by IR and UV techniques to provide a proof for the complexation of metal ions and to decide the structures and geometries of metal complexes on the basis of elemental analysis and magnetic properties of metal complexes.

Characterization of N, N′-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1, 2-diamine (3-MOBD MBn) Schiff Base
The 3-MOBDMBn Schiff base was obtained by refluxing 3-MOBD and MBn to produce a substantial yield (91.6 wt%; Scheme 1). The IR spectrum (Figure 2) of 3-MOBDMBn Schiff base showed absorption bands at 1609 cm\(^{-1}\) (>C=N), 1263 cm\(^{-1}\) (>C–O) phenolic and a broad band between 3200 and 2910 cm\(^{-1}\) was also observed, which was assigned to phenolic OH. The elemental analysis of 3-MOBDMBn Schiff base showed (wt %): C = 70.75, N = 7.17 and H = 5.68; Calcd (%): C = 69.82, N = 7.03 and H = 6.31, which corresponded to C\(_{23}\)H\(_{32}\)N\(_2\)O\(_4\) empirical formula of 3-MOBDMBn Schiff base.

Fig. 1: Thermal Stability of the 3-MOBDMBn Schiff base and its Copper Complex.

Scheme 1: Synthesis of N, N′-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MOBDMBn).
The molecular weight of Schiff base was 390.43 g mol\(^{-1}\) (Calcd 389.37 g mol\(^{-1}\)). The electronic spectra of 3-MOBdMBn Schiff base, using acetone as solvent, (Figure 3) showed absorption bands at 289 and 347 nm, which were assigned to \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions. The 1H-NMR spectrum of the Schiff base showed signals at \(\delta/\text{ppm} = 3.71(6\text{H}), 2.79(3\text{H}), 5.13(2\text{H}), 6.60(2\text{H}), 6.98(2\text{H}), 7.35(3\text{H}), 7.41(2\text{H}),\) and 8.61(2H) which corresponded to the structure of 3-MOBdMBn Schiff base.
Characterization of Copper Complex of 3-MOBdMBn Schiff Base

The loading of copper ion on 3-MOBdMBn Schiff base was carried out by refluxing Schiff base (Scheme 2) in solution of copper salt at 60 °C for 6 h. The copper complex of Schiff base (3-MOBdMBn-Cu) after separation and purification were analyzed for their structures and loading of copper ion. The complexation of copper(II) ion on 3-MOBdMBn Schiff base was 79.01 wt%.

The complexation of metal ions with 3-MOBdMBn Schiff base showed significant variations in IR bands for >C=N and >C–O groups and new absorption bands appeared due to the formation of M–O and M–N bonds in metal complexes. The disappearance of phenolic absorption band between 2910 and 3200 cm\(^{-1}\) in the IR spectrum of 3-MOBdMBn Schiff base after the complexation of metal ions was an evidence for the complexation of metal ions with 3-MOBdMBn Schiff base. On complexation with copper(II) ion, the frequency of >C=N absorption band of free Schiff base has decreased from 1609 to 1580 cm\(^{-1}\) (Figure 4). This shifting indicates the coordination of nitrogen with copper metal [20].

![Scheme 2. Loading of Copper ion on 3-MOBdMBn Schiff base.](image)

**Fig. 4:** FTIR Spectrum of 3-MHBdDBn-Cu Complex.
The new absorption band at 563 and 447 cm\(^{-1}\) for Cu–O bond and Cu–N bond, respectively indicate the complexation of copper metal with ligand [21–23] complexation of copper(II) ion showed (Table 1). The complexation of metal ions with Schiff base was further confirmed by comparing electronic spectra of metal complex and pure 3-MOBdMBn Schiff base. The complexation of copper(II) ion with 3-MOBdMBn Schiff base showed variation in \(\pi \to \pi^*\) transition from 289 to 282 nm, and for the \(n\to \pi^*\) transition was changed from 347 to 344 nm (Table 1). This variation indicates the complexation of copper metal [24]. The magnetic moment (\(\mu\)) of Schiff base complex of copper(II) ion was found to be 1.87 BM, which indicate the presence of one unpaired electron and paramagnetic nature of complex. These evidence shows \(t_{2g}^6 e_g^3\) electronic configuration correspond to square planar structure with dsp\(^2\) hybridization [25–26].

**Oxidation of Phenol**

The catalytic activity of copper complex of 3-MOBdMBn Schiff base was evaluated by studying the oxidation of phenol in the presence of hydrogen peroxide. The gas chromatographic analysis was used to determine the product selectivity and to estimate the percent conversion of phenol. The catechol was a major reaction product in the oxidation of phenol (Scheme 3). The formation of reaction products was attributed to enzymatic behavior of metal complexes of 3-MOBdMBn Schiff base.

### Table 1: FTIR frequencies and Electronic Transitions of 3-MOBdMBn Schiff base and its Copper Ion Complex.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Absorption frequencies/cm(^{-1})</th>
<th>Frequencies (\lambda_{\text{max}}/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(v_{C=N})  (v_{C=O}) (\nu_{\text{OH (phenolic)}}) (\nu_{M-O}) (\nu_{M-N})</td>
<td>(\pi \to \pi^<em>) (n\to \pi^</em>) (C \to T) d→d</td>
</tr>
<tr>
<td>3-MHBdMBn</td>
<td>1609 1263 2910-3200 - -</td>
<td>289 347 - 563 447</td>
</tr>
<tr>
<td>3-MHBdMBn-Cu</td>
<td>1580 1298 - - - -</td>
<td>282 344 360 563</td>
</tr>
</tbody>
</table>

**Scheme 3:** Oxidation of Phenol.
The conversion of phenol by copper catalyst was initially high at 240 min and then after the conversion became almost constant due to substantial decrease in the concentration of oxidant and substrate in the reaction mixture (Figure 5). The phenol conversion was 6.8% at 4 h without using the catalyst indicated in Figure 5.

The amount of phenol oxidized with hydrogen peroxide was almost equal to the sum of amount of catechol and hydroquinone produced, which discarded the formation of other reaction products such as polymeric phenols, but reaction showed high selectivity for catechol. The catalyst was recycled and also further evaluated for their catalytic activity after their applications in oxidation reactions. The efficiency of catalyst remained almost constant up to eight recycles (Table 2). The product selectivity remained unaffected on using recycled catalysts, which was an indication for the structural stability of metal complexes as confirmed by comparing IR spectra of recycled catalysts with IR spectra of freshly prepared catalysts. The rate of phenol conversion was $6.055 \times 10^{-6}$ moledm$^{-3}$s$^{-1}$ with turnover number 49.632 g mol$^{-1}$ Cu hr$^{-1}$ at the condition of 50 mmol of phenol, 50 mmol of hydrogen peroxide (30.0 wt%) and 50 mmol of catalyst at 30 min.

![Graph showing the effect of reaction time on oxidation of phenol](image)

**Fig. 5**: Effect of Reaction Time on Oxidation of Phenol.

**Table 2**: Efficiency of Recycled Catalysts 3-MHBdMBn-Cu in Oxidation of Phenol.

<table>
<thead>
<tr>
<th>Metal complexes</th>
<th>Recycle number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>3-MHBdMBn -Cu</td>
<td>Conversion</td>
</tr>
<tr>
<td></td>
<td>Selectivity</td>
</tr>
</tbody>
</table>

[Phenol]:[Catalyst]: [H$_2$O$_2$] = 1:1:1 (0.05M), Temp. = 70$^\circ$C. CH$_3$CN = 2.0 mL.
CONCLUSION
This research paper describes the synthesis and characterizations of a new Schiff base derived from 2-hydroxy-3-methoxybenzaldehyde (3-MOBd) and 4-Methylbenzene-1, 2-diamine (MBn) and its copper complex. The spectral data reveal a square planar geometry for the copper(II) complex with a tetradentate ligand. The catalytic activity of the prepared copper complex was studied in the oxidation of phenol using hydrogen peroxide as an oxidant. Catechol and hydroquinone are the sole products of the reaction. The oxidation of phenol showed high selectivity for catechol. The oxidation of phenol was maximum at the condition of 50 mmol of phenol, 50 mmol of hydrogen peroxide (30.0 wt%) and 50 mmol of catalyst. The activity of the catalyst increased with increase in time but after 240 min the conversion of phenol remains all most constant.

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REFERENCES
Preparation, characterization, and catalytic studies of Iron and Cobalt complexes supported by ONNO – Tetradentate Schiff-Base ligands

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Abstract: The free and polymer anchored complexes of iron and cobalt [3-MHBdMBn-M and P-3-MHBdMBn-M], supported by ONNO-tetradentate Schiff-base ligands are prepared by the reactions of metal solution with one molar equivalent of unsupported 3-MHBdMBn (N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine) or polymer supported (P-3-MHBdMBn) Schiff-base ligands in methanol. The structural study reveals that iron(III) complex of 3-MHBdMBn Schiff base is octahedral in geometry, whereas, cobalt(II) ions complexes is square planar. Complexation of metal ions increased the thermal stability of 3-MHBdMBn Schiff base. The catalytic activities of metal complexes towards the oxidation of phenol are investigated in the presence of hydrogen peroxide. Experimental results indicate that the reactivity of P-3-MHBdMBn-M is dramatically affected by the polymer support over 3-MHBdMBn-M and iron complexes have greater activity than the cobalt analogue.

Keywords: Schiff Base, Polymer Support, Catalysis, Metal Complexes, Phenol, Oxidation

1. Introduction

Schiff base complexes of transition metal ions has shown high catalytic activities in various chemical reactions such as oxidation, [1,2] epoxidation of olefins, [3] and polymerization of ethylene to obtain narrow molecular weight distribution, [4,5]. However, the polymer-supported analogues of metal complexes showed high catalytic activity [2,3,6-8], and enantioselectivity [6] in comparison to homogeneous catalysts. The manganese (II) salen complexes anchored on tailor-made polymers have more enantioselectivity without any mass transfer limitation for alkenes on polymer supports [9]. The metal complexes were also anchored on other supports, [10-13] but it has been studied that polymeric supports provided better control on efficiency of catalysts [6] due to microenvironment provided by polymer chains for the substrates in comparison to zeolites [14] and silica [15]. The metal complexes on solid supports are immobilized either physically or by forming a covalent bond between metal complexes and supports [6]. Further, the recovery of physically linked catalysts has been found to be low in comparison to covalently bound catalysts due to the leaching of catalysts. The oxidation of phenol using unsupported Schiff base complexes of metal ions is reported [16], but the oxidation of phenol using polymer-supported transition metal complexes was found to be high [17] in the presence of tert-butyl hydroperoxide (t-BHP). The polymer-supported Schiff base complexes of metal ions also showed variations in the decomposition of hydrogen peroxide with their redox potentials [18], which provided a useful criterion to explain the activity of metal ions in the oxidation of phenol in the presence of hydrogen peroxide as the oxidant. The activity of polymer-supported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions in the oxidation of phenol [19-20] also showed variation with temperature, time, etc, which might be due to the change in concentration of substrate or catalyst. The oxidation of phenol in the presence of metal complexes of
Salen and hydrogen peroxide as the oxidant is reported, but catalytic activity of metal complexes of N,N′-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MHBDMBn) Schiff base is not reported in the literature; hence, in these investigations an attempt has been made to prepare polymer-supported metal complexes of 3-MHBDMBn Schiff base and to characterize them for their structures and catalytic activity towards the oxidation of phenol in the presence of hydrogen peroxide as an oxidant.

2. Experimental

2.1. Materials

Divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai, India and used to anchor synthesized 3-MHBDMBn Schiff base complexes of metal ions. The chloro salts of iron(III) and cobalt(II) ions were purchased from Ranbaxy, Mumbai, India and used without further purifications. The phenol, hydrogen peroxide (30.0 wt%), 2-hydroxy-3-methylbenzaldehyde (3-MHBD) and 4-Methylbenzene-1,2-diamine (MBn) were procured from E. Merck, India. Other chemicals and solvents were of analytical grade (>99.0 wt%) and used after purifications with standard methods [21].

2.2. Characterization of 3-MHBDMBn Schiff Base and Its Metal Complexes

IR spectra of 3-MHBDMBn Schiff base and its metal complexes were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of 3-MHBDMBn Schiff base and its metal complexes were recorded with Shimadzu 1601 PC UV–Vis Spectrophotometer by using sample mull in a cuvette. Thermo gravimetric analysis (TGA) of 3-MHBDMBn Schiff base and its metal complexes was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10°C min⁻¹. The loading of metal ions on 3-MHBDMBn Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_max of corresponding metal ions. The amount of 3-MHBDMBn Schiff base anchored on polymer beads and its composition were estimated using Haraeus Carlo Erba 1108 Elemental Analyzer. The ¹H-NMR spectra of 3-MHBDMBn Schiff base and its metal complexes were recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d₆ as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (μ) of metal complexes was measured using Vibrating Sample Magnetometer-155. The molecular weight of 3-MHBDMBn Schiff base and its metal complexes was determined using a Vapor Pressure Osmometer (Merck VAPRO 5600, Germany).

2.3. Synthesis of N, N′-Bis (2-Hydroxy-3-Methyl Benzaldehyde)4-Methylbenzene-1,2-diamine Schiff Base (3-MHBDMBn) and Its Metal Complexes

3-MHBDMBn Schiff base was synthesized by the modified procedure reported in the literature [21]. The reaction mixture containing 2-hydroxy-3-methylbenzaldehyde (20.00 mmol, 2.72 g) and 4-Methylbenzene-1,2-diamine (10.00 mmol, 1.22 g) in methanol was refluxed at 60°C for about 1 hr. The reaction mixture on cooling at low temperature produced light orange colored crystals, which were filtered and recrystallized with methanol. The metal complexes of 3-MHBDMBn Schiff base were prepared taking 100 ml methanolic solution of mixture of Schiff base (20.00 mmol, 7.16 g) and 20.00 mmol of metal ions in a round bottom flask and refluxing at 60°C. After 8 h, the solution was cooled and crystalline metal complexes were separated from the mother liquor. Finally, metal complexes were recrystallized in methanol and dried in a vacuum desiccator.

2.4. Synthesis of Polymer-Anchored N, N′-Bis (2-Hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1,2-Diamine (P-3-MHBDMBn) Schiff Base and Its Metal Complexes

To prepare polymer-anchored metal complexes of 3-MHBDMBn Schiff base, the N, N′-bis (4-amino-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (A-3-MHBDMBn) Schiff base was prepared by carrying out nitrosation and reduction reactions on 3-MHBDMBn Schiff base and then reacting resulted A-3-MHBDMBn Schiff base with cross-linked chloromethylated polystyrene beads. The nitrosation of 3-MHBDMBn Schiff base was carried out using 20.00 mmol (7.16 g) of 3-MHBDMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at -5°C. The resultant N, N′-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-3-MHBDMBn) was filtered and washed with hot and cold water to remove reaction impurities. The reduction of NO-3-MHBDMBn was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of metallic iron, which produced A-3-MHBDMBn Schiff base. To immobilize the prepared A-3-MHBDMBn Schiff base on cross-linked chloromethylated polystyrene, the methanol swollen polymer beads (5.0 g) were refluxed in 50 ml methanol containing 20.00 mmol (7.76 g) A-3-MHBDMBn Schiff base. After 8 h, the A-3-MHBDMBn Schiff base-anchored polymer beads were separated and dried in a vacuum desiccator. The amount of A-3-MHBDMBn Schiff base loaded on polymer beads was estimated with elemental analysis. Subsequently, the metal ions were loaded by keeping 3-MHBDMBn loaded polymer beads (5.0 g) for 10 h in an aqueous solution (50 ml) of metal ions (20.00 mmol). 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 on polymer beads was determined by analyzing the loading solution with an Atomic Absorption Spectrometer. The loading of metal ions on free and polymer-supported 3-MHBdMBn Schiff base was calculated as complexation of metal ions using the amount of 3-MHBdMBn Schiff base taken initially and the amount of metal ions loaded on polymer beads.

\[
\text{Complexation of metal ions} = \frac{\text{Amount of metal ions loaded}}{\text{Amount of Schiff base used for loading}} \times 100
\]

2.5. Catalytic Activity of Metal Complexes in Oxidation of Phenol

To evaluate the catalytic activity of free and polymer-supported metal complexes of 3-MHBdMBn Schiff base, the oxidation of phenol was carried out using hydrogen peroxide as the oxidant at fixed ionic strength (0.10 M) and hydrogen ions concentration (pH 7.0) in the reaction mixture. To carry out these reactions, a calculated amount of metal-anchored polymer beads were taken in a two-necked round-bottomed flask containing 0.05 M phenol (4.70 g). The oxidation of phenol was carried out by adding 5.67 g (0.05 M) hydrogen peroxide (30.0 wt%) in the reaction mixture and 2.0 ml chlorobenzene as an internal standard. The water condenser and supply of nitrogen were attached with reaction flask before starting the heating and stirring (1200 rpm) of reaction mixture. Gas chromatography was used to follow these reactions at different time intervals. The retention time of standards was used to identify the reaction products, and product selectivity was measured using peak areas of reaction products in the chromatograms. The reactions were also carried out taking different molar ratios of substrates, hydrogen peroxide, and catalyst. The rate of oxidation for the oxidation of phenol was determined by studying reactions at different temperatures and at constant molar ratios of substrate to H\(_2\)O\(_2\) and catalyst. The reactions were also studied without using catalysts to analyze the effect of catalysts in the oxidation of phenol.

3. Results and Discussion

Investigations have revealed that polymer-supported metal complexes are sometimes more catalytic and efficient than free and unsupported analogs [38]. The activity of catalysts also showed dependence on properties of polymer supports [39] and amount of loaded catalysts [40,41]. Thermal stability of catalysts is required to be high, if these catalysts have to be applied in high temperature reactions. Therefore, thermal analysis of supported metal complexes was carried out to evaluate their possible applications in high temperature reactions and to prove a method for the complexation of metal ions with polymer-anchored 3-MHBdMBn Schiff base. The TGA of polymer supported 3-MHBdMBn Schiff base showed a weight loss of 40.4 wt% at 500°C, but its iron(III) and cobalt(II) ion complexes showed a weight loss of 25.2 and 35.1 wt%, respectively at same temperature, which was clear indication that iron(III) ion complexes were more stable in comparison to cobalt(II) ions (Figure 1). The weight loss at 500°C was attributed to the decomposition of metal complexes of 3-MHBdMBn Schiff base.

In addition to thermal analysis, the free and polymer-supported metal complexes of 3-MHBdMBn Schiff base were also characterized by IR and UV techniques to provide a proof for the complexation of metal ions and to decide the structures and geometries of metal complexes on the basis of elemental analysis and magnetic properties of metal complexes.

![Figure 1. Thermal stability of polymer-supported 3-MHBdMBn Schiff base and its metal complexes](image)

3.1. Characterization of N, N'-Bis (2-hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1, 2-Diamine (3-MHBd MBn) Schiff base

The 3-MHBdMBn Schiff base was obtained by refluxing 2-hydroxy-3-methylbenzaldehyde (3-MHBd) and 4-Methylbenzene-1,2-diamine (MBn) for 1hr at 60°C in methanol, which produced a substantial yield (86.2 wt%) (Scheme 1). The IR spectrum (Figure 2) of 3-MHBdMBn Schiff base showed absorption bands at 1610 cm\(^{-1}\) (>C–O), 3286 cm\(^{-1}\) (>C–O) phenolic (Figure 2) and a broad band between 3350 and 2910 cm\(^{-1}\) was also observed, which was assigned to phenolic OH. The elemental analysis of 3-MHBdMBn Schiff base showed (wt%): C = 76.64, N = 5.15, and H = 7.27. The electronic spectra of 3-MHBdMBn Schiff base (Figure 3) showed absorption bands at 284 nm and 346 nm, which were assigned to π → π* transitions. The 1H-NMR spectrum of the Schiff base showed signals at δ/ppm = 2.52(6H), 2.83(3H), 3.15(2H), 6.91(2H), 7.27(2H), 7.41(3H), and 7.60(2H), and...
8.66(2H) which corresponded to the structure of 3-MHbDMBn Schiff base.

3.2. Synthesis and Characterization of N, N’-bis (4-Amino-2-Hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1, 2-Diamine (A-3-MHbDMBn) Schiff Base and Its Anchoring on Polymer Beads

The nitrosation of 3-MHbDMBn Schiff base was carried out in the presence of NaNO₂/HCl, which gave 86.5% yield of N, N’-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-3-MHbDMBn) (Scheme 2). The elemental analysis of N, N’-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine showed (wt%): C = 67.00, N = 12.63, and H = 5.00; Calcd (wt%): C = 66.34, N = 13.45, and H = 4.84, which corresponded to C_{23}H_{20}N_{4}O_{4} formula of nitrosated Schiff base. The molecular weight of NO-3-MHbDMBn was 415.03 g mol⁻¹ (Calcd 416.43 g mol⁻¹). The IR spectrum of NO-3-MHbDMBn showed absorption bands at 1607 cm⁻¹ (>C=N), 1266 cm⁻¹ (>C–O)phenolic, and 1530 cm⁻¹ and 1320 cm⁻¹ for N–O group. The nitrosation of 3-MHbDMBn Schiff base showed a shift in NMR signals in comparison to NMR signals observed with pure 3-MHbDMBn Schiff base. The nitrosated 3-MHbDMBn Schiff base showed proton signals at δ/ppm = 2.54(6H), 2.88(3H), 5.15(2H), 7.35(2H), 7.42(3H), 7.96(2H), and 8.69(2H), which corresponded to the structure of nitrosated 3-MHbDMBn Schiff base. The protons ortho to nitroso group in 3-MHbDMBn Schiff base were deshielded; hence, their signals appeared at 7.35 and 7.96 ppm in place of 7.27 and 7.60 ppm respectively, of pure 3-MHbDMBn Schiff base. The proton signal at 6.91 ppm was missing due to the substitution of nitroso group in the benzene. The NO-3-MHbDMBn was reduced with iron(III) ions in the presence of hydrochloric acid, which gave 81.3 wt% yield of A-3-MHbDMBn Schiff base. The elemental analysis of A-3-MHbDMBn Schiff base showed (wt%): C = 70.54, N = 13.00, and H = 7.02, Calcd (wt%): C = 71.11, N = 14.42, and H = 6.23, which corresponded to C_{23}H_{24}N_{4}O_{2} empirical formula of Schiff base. The molecular weight of A-3-MHbDMBn Schiff base was found to be 387.23 g mol⁻¹ (Calcd 388.46 g mol⁻¹). The IR spectrum of A-3-MHbDDBn Schiff base showed absorption bands at 1605 cm⁻¹ (>C=N), 1263 cm⁻¹ (>C–O)phenolic, and a band between 1632 and 1618 cm⁻¹ for >C–N group. The 1H-NMR spectrum of A-3-MHbDDBn Schiff base showed proton signals at δ/ppm = 2.52(6H), 2.85(3H), 4.15 (4H), 5.15(2H), 6.36 (2H), 7.42(3H), 6.81(2H), and 8.69(2H), which corresponded to the structure of A-3-MHbDDBn Schiff base.
The synthesized Schiff base was anchored on cross-linked chloromethylated polystyrene beads by refluxing A-3-MHBdMBn Schiff base with polymer beads in DMF for 8 h at 60°C. The amount of A-3-MHBdMBn Schiff base anchored on polymer beads was 87.0 wt% (Scheme 3). The anchoring of A-3-MHBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of 3-MHBdMBn Schiff base anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1602 cm\(^{-1}\) (\(>\text{C=N}\)), 1260 cm\(^{-1}\) (\(>\text{C–O}\) phenolic), and a broadband between 1629 and 1610 cm\(^{-1}\) (\(>\text{C=N}\)), which were absent in the IR spectrum of pure polymer beads, but were present in free Schiff base. The IR spectrum of pure polymer beads showed absorption band at 1262 cm\(^{-1}\), which is attributed to C–Cl bond of chloromethyl in cross-linked polymer beads. The decrease in the intensity of absorption band at 1262 cm\(^{-1}\) in polymer-anchored 3-MHBdMBn Schiff base than pure polymer beads was an evidence for anchoring of 3-MHBdMBn Schiff base on polymer beads. The appearance of new absorption bands and shift in characteristic absorption bands of 3-MHBdMBn Schiff base were also used as evidence for anchoring of 3-MHBdMBn Schiff base on polymer beads.

3.3. Characterization of Free and Polymer-Anchored Metal Complexes of 3-MHBdMBn Schiff base

The loading of metal ions on free and polymer-supported 3-MHBdMBn Schiff base was carried out by refluxing free Schiff base (Scheme 4) and polymer-anchored Schiff base in solution of metal salt at 60°C for 6 h (Scheme 5). The metal complexes of free Schiff base (3-MHBdMBn-M) and polymer-anchored Schiff base (P-3-MHBdMBn-M) after separation and purification were analyzed for their structures and loading of metal ions. The complexation of iron(III) ions on free 3-MHBdMBn Schiff base and polymer-anchored Schiff base was 77.71 and 82.81 wt%, whereas for cobalt(II) ions 74.85 and 83.99 wt% respectively (Table 1). These results have clearly suggested that the loading of metal ions on polymer-supported 3-MHBdMBn Schiff base was higher than free 3-MHBdMBn Schiff base.
The complexation of metal ions with 3-MHBdMBn Schiff base showed significant variations in IR bands for >C=N and >C–O groups and new absorption bands appeared due to the formation of M–O and M–N bonds in metal complexes. The disappearance of phenolic absorption band between 2910 and 3350 cm⁻¹ in the IR spectrum of 3-MHBdMBn Schiff base after the complexation of metal ions was an evidence for the complexation of metal ions with 3-MHBdMBn Schiff base. The polymer-supported Schiff base showed absorption bands at low frequency (Figure 4). On complexation with iron(III) ions, the frequency of >C=N absorption band of free Schiff base has decreased from 1610 to 1605 cm⁻¹, whereas polymer-supported Schiff base showed variation from 1602 to 1601 cm⁻¹ (Figure 4).

Complexation of cobalt(II) with free Schiff base and polymer-supported Schiff base showed absorption bands at 1593 cm⁻¹ and 1589 cm⁻¹, respectively (Figure 4). These variations in IR band corresponding to >C=N group of 3-MHBdMBn Schiff base were used as evidence for interactions of metal ions with azomethine nitrogen (>C=N) of 3-MHBdMBn Schiff base. The complexation of iron(III) ions showed new absorption band at 424 cm⁻¹ with free Schiff base and at 420 cm⁻¹ with polymer-anchored Schiff base, which was due to the formation of M–N bond between iron(III) ions and Schiff base. The complexation of cobalt(II) ions showed absorption band at 416 cm⁻¹ for M–O bond with free and polymer-supported 3-MHBdMBn Schiff base. The complexation of iron(III) and cobalt(II) ions showed another new band due to the formation of bond between metal ions and phenolic oxygen (–O–M). The complexation of iron(III) and cobalt(II) ions with polymer-supported 3-MHBdMBn Schiff base produced O–M absorption band at 537 cm⁻¹ and 559 cm⁻¹ (Figure 4). The completion of metal ions with Schiff base was further confirmed by comparing electronic spectra of metal complexes and pure 3-MHBdMBn Schiff base.

The magnetic moment (µ) of Schiff base complexes of iron(III) and cobalt(II) ions was found to be 1.99 and 1.86 BM, respectively, which indicated that iron(III) and cobalt(II) ions complexes were paramagnetic in nature with one unpaired electron in each. The magnetic moment (µ) and electronic configurations have suggested an octahedral structure with d²sp³ hybridization for iron(III) ions complexes and square planar structure with dsp² hybridization for cobalt(II) ions complexes (Scheme 6).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>π→π*</th>
<th>n→π*</th>
<th>C→T</th>
<th>d→d</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-MHBdMBn</td>
<td>284</td>
<td>346</td>
<td>-</td>
<td>459</td>
</tr>
<tr>
<td>P-3-MHBdMBn</td>
<td>281</td>
<td>341</td>
<td>-</td>
<td>451</td>
</tr>
<tr>
<td>3-MHBdMBn-Fe</td>
<td>254</td>
<td>310</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-3-MHBdMBn-Fe</td>
<td>251</td>
<td>305</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-MHBdMBn-Co</td>
<td>243</td>
<td>299</td>
<td>363</td>
<td>-</td>
</tr>
<tr>
<td>P-3-MHBdMBn-Co</td>
<td>239</td>
<td>293</td>
<td>352</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Efficiency of complexation (EC) of metal ions (wt%)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Unsupported 3-MHBdMBn Schiff base</th>
<th>Polymer supported 3-MHBdMBn Schiff base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III) ions</td>
<td>77.71</td>
<td>82.81</td>
</tr>
<tr>
<td>Co(II) ions</td>
<td>74.85</td>
<td>83.99</td>
</tr>
</tbody>
</table>


Table 2. Electronic transitions in unsupported and polymer supported metal ions complexes of 3-MHBdMBn Schiff base

![Figure 4. FTIR spectra of polymer supported 3-MHBdDBn-Fe complex (A) and polymer supported 3-MHBdDBn-Co complex](image)

The magnetic moment (µ) of Schiff base complexes of iron(III) and cobalt(II) ions was found to be 1.99 and 1.86 BM, respectively, which indicated that iron(III) and cobalt(II) ions complexes were paramagnetic in nature with one unpaired electron in each. The magnetic moment (µ) and electronic configurations have suggested an octahedral structure with d²sp³ hybridization for iron(III) ions complexes and square planar structure with dsp² hybridization for cobalt(II) ions complexes (Scheme 6).

![Scheme 6. Geometry and structure of 3-MHBdMBn Schiff base complexes of metal ions](image)
3.4. Oxidation of Phenol

The catalytic activity of free and polymer-supported metal complexes of 3-MHBdMBn Schiff base was evaluated by studying the oxidation of phenol in the presence of hydrogen peroxide. The gas chromatographic analysis was used to determine the product selectivity and to estimate the percent conversion of phenol. The catechol (CTL) was a major reaction product in the oxidation of phenol (Scheme 7). The formation of reaction products was attributed to enzymatic behavior of metal complexes of 3-MHBdMBn Schiff base.

\[
\text{Scheme 7. Oxidation of phenol}
\]

The polymer support has facilitated the decomposition of these intermediates; hence, per cent conversion of phenol was more with polymer-supported metal complexes (Figure 5) in comparison to free metal complexes of 3-MHBdMBn Schiff base (Table 3). The conversion of phenol was initially high at 240 min and then after the conversion became almost constant due to substantial decrease in the concentration of oxidant and substrate in the reaction mixture (Table 3). Similar trends in substrate conversion were observed with supported catalysts at different time intervals as found with unsupported catalysts (Figure 5). The oxidation reaction also shown dependence on type of catalyst as it is clear from substrate conversion in the presence of 3-MHBdMBn Schiff base complexes of iron(III), and cobalt(II) ions (Table 3). The percent conversion of phenol was more with Schiff base complexes of iron(III) ions in comparison to cobalt(II) ion complex. The high activity of metal complexes on polymer support was due to the facile interactions of catalyst with substrate than 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 sum of amount of CTL and hydroquinone (HQ) produced, which discarded the formation of other reaction products such as polymeric phenols.

The amount of CTL and HQ was equal to phenol conversion, but reaction showed high selectivity for CTL. The supported catalysts were recycled and also further evaluated for their catalytic activity after their applications in oxidation reactions. The efficiency of supported catalysts remained almost constant up to six recycles and then the efficiency decreased (Table 4). The product selectivity for CTL remained unaffected on using recycled catalysts, which was an indication for the structural stability of metal complexes on polymer support as confirmed by comparing IR spectra of recycled catalysts with IR spectra of freshly prepared catalysts. The activity of metal complexes in substrate conversion and product selectivity was evaluated at different molar ratios of substrate to hydrogen peroxide and catalyst.

\[
\text{Figure 5. Effect of reaction time on oxidation of phenol in presence of polymer-supported metal complexes. [Phenol]}/[\text{Catalyst}]/[\text{H}_2\text{O}_2] = 1:1:1 (0.05M), \text{Temp.} = 70 \degree \text{C}.
\]

The rate of phenol conversion was high (2.41 x 10^{-6} \text{ mole dm}^{-3} \text{ s}^{-1}) in the presence of polymer-supported 3-MHBdMBn Schiff base complexes of iron(III) ions than Schiff base complexes of cobalt(II), which showed the rate of phenol conversion as 1.79 x 10^{-6} \text{ mole dm}^{-3} \text{ s}^{-1} (Table 5). The rate of phenol conversion and selectivity for CTL was low with free 3-MHBdMBn Schiff base complexes of metal ions. The turnover number (TON) for the oxidation of phenol was high (16.33 g mol^{-1} \text{Fe hr}^{-1}) in the presence of 3-MHBdMBn Schiff base complexes of iron(III) ions in comparison to Schiff base complexes of cobalt(II) (12.14 g mol^{-1} \text{Co hr}^{-1}) at a molar ratio of 1:1:1 of H_2O_2 to phenol and catalyst (Table 5). The rate of substrate conversion and TON in the oxidation of phenol varied significantly with molar ratio of hydrogen peroxide but product selectivity in both cases remained almost constant (Tables 5).

\[
\text{Table 3. Catalytic activity of unsupported metal complexes (M-3-MHBdMBn) in oxidation of phenol (Ph)}
\]

<table>
<thead>
<tr>
<th>Time/min</th>
<th>Percent conversion (wt%) of Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-3-MHBdMBn</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>7.4</td>
</tr>
<tr>
<td>30</td>
<td>12.9</td>
</tr>
<tr>
<td>45</td>
<td>20.6</td>
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<tr>
<td>60</td>
<td>27.2</td>
</tr>
<tr>
<td>90</td>
<td>42.0</td>
</tr>
<tr>
<td>240</td>
<td>48.4</td>
</tr>
<tr>
<td>720</td>
<td>49.9</td>
</tr>
<tr>
<td>1440</td>
<td>51.0</td>
</tr>
</tbody>
</table>

[Phenol]}/[\text{Catalyst}]/[\text{H}_2\text{O}_2] = 1:1:1 (0.05M), \text{Temp.} = 70 \degree \text{C. CH}_2\text{CN} = 2.0 \text{ mL.}
Table 4. Efficiency of recycled supported catalysts (P-3-MHBdMBn-M) in oxidation of phenol.

<table>
<thead>
<tr>
<th>Supported metal complexes</th>
<th>Recycle number</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-3-MHBdMBn -Fe</td>
<td>Conversion</td>
<td>72.3</td>
<td>72.0</td>
<td>71.7</td>
<td>68.0</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td>Selectivity</td>
<td>95.1</td>
<td>95.3</td>
<td>95.1</td>
<td>92.3</td>
<td>90.1</td>
</tr>
<tr>
<td>P-3-MHBdMBn-Co</td>
<td>Conversion</td>
<td>53.6</td>
<td>53.1</td>
<td>52.4</td>
<td>50.2</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td>Selectivity</td>
<td>93.8</td>
<td>93.9</td>
<td>92.7</td>
<td>90.4</td>
<td>88.0</td>
</tr>
</tbody>
</table>

[Phenol]:[Catalyst]: [H$_2$O$_2$] = 1:1:1 (0.05M), Temp. = 70°C, CH$_3$CN = 2.0 mL

Table 5. Oxidation of phenol by metal ions complexes of polymer supported 3-MHBdMBn Schiff base: Phenol conversion, selectivity for catechol and kinetic parameters

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Conversion (wt%)</th>
<th>Selectivity (wt%)</th>
<th>TON</th>
<th>Rp</th>
<th>Conversion (wt%)</th>
<th>Selectivity (wt%)</th>
<th>TON</th>
<th>Rp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>50.5</td>
<td>96.5</td>
<td>11.37</td>
<td>1.68</td>
<td>72.3</td>
<td>95.3</td>
<td>16.33</td>
<td>2.41</td>
</tr>
<tr>
<td>Cobalt</td>
<td>35.2</td>
<td>90.3</td>
<td>7.63</td>
<td>1.13</td>
<td>53.6</td>
<td>93.9</td>
<td>12.14</td>
<td>1.79</td>
</tr>
</tbody>
</table>

[H$_2$O$_2$]/[Phenol]/[Catalyst]= 0.05M, Time = 1440 min, Temp. = 70°C, CH$_3$CN = 2.0 mL TON in terms of = g mol$^{-1}$M hr$^{-1}$, Rate of oxidation (Rp) in terms of = 10$^6$ mole dm$^{-3}$ s$^{-1}$

3.5. Mechanism for Oxidation of Phenol

Considering the experimental findings for the oxidation of phenol with free and supported 3-MHBdMBn Schiff base complexes of metal ions, the following reaction steps are proposed (Scheme 8). The free and polymer-supported Schiff base complexes of metal ions (3-MHBdMBn-M) have produced active species (M-3-MHBdMBn-HOO$^-$) through fast interactions with hydrogen peroxide and 3-MHBdMBn Schiff base. The active species was subsequently used in the formation of intermediates ((M-3-MHBdMBn-Ph-HOO$^-$) through its interactions with phenol in a rapid equilibrium (k). The intermediate (M-3-MHBdMBn-Ph-HOO$^-$) has facilitated the nucleophilic attack of OOH species on ortho and para position on phenol to produce hydroxy-substituted phenols (Scheme 7). The reaction products, catalyst and hydroxyl ions were formed through decomposition of intermediates (Scheme 8 step 4) and finally the hydroxyl ions reacted with hydrogen ions, which were produced in step 1.

4. Conclusion

The polymer-supported transition metal complexes of 3-MHBdMBn Schiff base were synthesized and characterized successfully for their structures and catalytic activity in the oxidation of phenol. The polymer-supported 3-MHBdMBn Schiff base complexes of metal ions showed high catalytic activity than free metal complexes. The Schiff base complexes of iron(III) ions were more active in the conversion of phenol than cobalt(II) ions. The oxidation of phenol showed high selectivity for CTL. The supported catalysts showed high rate of oxidation and TON than unsupported catalysts, which clearly suggested that polymer support has played a significant role in increasing the rate for oxidation of phenol in the presence of metal complexes of 3-MHBdMBn Schiff base.

Acknowledgments

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References


Polymer Anchored Copper (II) Complex Supported by -ONNO- Schiff Base: Efficient Catalysts for Oxidation of Phenol

**KEYWORDS**
- Schiff base; polymer support; catalysis; organometallic; phenol; oxidation

**INTRODUCTION**

Transition-metal Schiff base complexes have shown significant catalytic activities in various reactions such as oxidation,[1] epoxidation of olefins,[2] polymerization of ethylenes,[3] etc. but supported metal-ion complexes have shown high catalytic activity in comparison with unsupported catalysts. [4-6]. Although metal ion complexes have been immobilized on various supports [7-8], their activity on polymer supports is quite high [9] because of the dynamic microenvironment [10] and liquid-phase conditions [11], in which an anchored catalyst is able to perform rotational and translational motions. The homogeneity of catalysts on zeolite [12] and silica [13] supports is significantly different from that on polymer supports. The Schiff base complexes of metal ions have been used in the oxidation of phenols [14], but the oxidation of phenol with polymer-supported transition-metal-ion complexes has been found to be higher. [15]

On the other hand removal of environmental pollutants such as phenol through oxidation processes is an approach that is attracting receives increasing attention [16]. The general methods of phenol removal, that include sorption over natural surfaces like activated carbon [17], or sorption over organophilic clay that was modified with organic polymers [18] exist, is not always enough and thus, the phenol need to oxidize or reduce them to less harmful products is necessary. Oxidation of phenols using various chemical reagents such as, hydrogen peroxide, permanganate, molecular oxygen and ozone, are widely used [19]. The use of hydrogen peroxide has the advantage of producing oxygen and can be used to augment biological degradation [20]. Besides, the adoption of H$_2$O$_2$ as an alternative of current industrial oxidation processes offers environmental advantages, some of which are: (a) replacement of stoichiometric metal oxidants; (b) replacement of halogens; (c) replacement or reduction of solvent usage; and (d) avoidance of salt by-products. Iron is the most common homogeneous catalyst for hydrogen peroxide [21]. Heterogeneous catalysts involve metal oxides [23], and polymeric supports [24-25].

The activity of polymer-supported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions in the oxidation of phenol [26-27] also showed variation with temperature, time, etc., which might be due to the change in concentration of substrate or catalyst. Although the oxidation of phenol with H$_2$O$_2$ in the presence of metal-ion complexes of salen have been reported, the catalytic activity of metal-ion complexes of the HMBdMBn (N, N’-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine) Schiff base has not been reported in the literature; hence, attempts have been made to synthesize and characterize polymer-supported Cu(II) complex of the HMBdMBn Schiff base and to evaluate their catalytic activity in the oxidation of phenol in the presence of H$_2$O$_2$ as an oxidant in comparison with unsupported HMBdMBn Schiff base analogue complexes.

**EXPERIMENTAL**

2.1 Materials

Divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai. The copper(II) chloride anhydrous was purchased from Hi-Media Laboratories Pvt. Ltd, Mumba. The phenol, hydrogen peroxide (30.0 wt%), 2-hydroxy-3-methylbenzaldehyde and 4-Methylbenzene-1,2-diamine were procured form E. Merck, India. Other chemicals and solvents were of analytical grade (>99.0 wt %) and used after purifications with standard methods [28].

2.2 Characterization of the HMBdMBn Schiff base and its copper(II) ion complex

FTIR spectra of HMBdMBn Schiff base and its copper complex were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of was recorded with Shimadzu 1601 PC UV–Vis Spectrophotometer. Thermo gravimetric analysis(TGA) was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10$^\circ$C min$^{-1}$. The 1H-
NMR spectra was recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d$_6$ as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (µ) of copper complex was measured using Vibrating Sample Magnetometer-155. The molecular weight of Schiff base and its copper complex was determined using a Vapor Pressure Osmometer (Merck VAPRO 5600, Germany).

2.3 Synthesis of HMBdMBn Schiff base and its copper complex

HMBdMBn Schiff base was synthesized by the modified procedure reported in the literature [28]. The reaction mixture containing 2-hydroxy-3-methylbenzaldehyde (20.00 mmol, 2.72 g) and 4-Methylbenzene-1,2-diamine (10.00 mmol, 1.22 g) in methanol was refluxed at 60°C for about 1 h. The reduction mixture on cooling at low temperature produced light orange colored crystals, which were filtered and recrystallized with methanol. The copper complex of HMBdMBn Schiff base was prepared taking 20.00 ml methanolic solution of mixture of Schiff base (20.00 mmol, 7.16 g) and 20.00 mmol of copper ion in a round bottom flask and refluxing at 60°C. After 8 h, the solution was cooled and copper complex was separated from the mother liquor. All reactions were performed under nitrogen atmosphere. Finally, copper complex was recrystallized in methanol and dried in a vacuum desiccator.

2.4 Synthesis of polymer-anchored HMBdMBn Schiff base and its copper complex

For the preparation of polymer-anchored copper complex of HMBdMBn Schiff base, the N, N'-bis-(4-amino-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base was prepared by carrying out nitrosation and reduction reactions on HMBdMBn Schiff base and then reacting resulted A-HMBdMBn Schiff base with cross-linked chloromethyl polystyrene beads. The nitrosation of HMBdMBn Schiff base was carried out using 20.00 mmol (7.16 g) of HMBdMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at -5°C. The resultant NO-HMBdMBn Schiff base was filtered and washed with hot and cold water to remove reaction impurities. The reduction of NO-HMBdMBn Schiff base was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of metallic iron, which produced A-HMBdMBn Schiff base. To immobilize the prepared A-HMBdMBn Schiff base on cross-linked chloromethylated polystyrene, the methanol swollen polymer beads (5.0 g) were refluxed in 50 ml methanol containing 20.00 mmol (7.76 g) A-HMBdMBn Schiff base. After 8 h, the HMBdMBn Schiff base-anchored polymer beads were separated and dried in a vacuum desiccators and the copper ion was loaded by keeping HMBdMBn loaded polymer beads (5.0 g) for 10 h in an aqueous solution (50 ml) of copper ion (20.00 mmol). 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 copper ion on free and polymer-supported HMBdMBn Schiff base was calculated as follows.

Complexation of copper ion = Amount of copper ion loaded Amount of Schiff base used for loading X 100

2.5 Catalytic activity of copper complex in oxidation of phenol

For the evaluation of catalytic activity of free and polymer-supported copper complex of HMBdMBn Schiff base, the oxidation of phenol was carried out using hydrogen peroxide as the oxidant at fixed ionic strength (0.10 M) and hydrogen ions concentration (pH 7.0) in the reaction mixture. To carry out these reactions, a calculated amount of copper-anchored polymer beads were taken in a two-necked round-bottomed flask containing 0.05 M phenol (4.70 g). The oxidation of phenol was carried out by adding 3.67 g (0.05 M) hydrogen peroxide (30.0 wt%) in the reaction mixture and 2.0 mL acetonitrile as an internal standard. The water condenser and supply of nitrogen were attached with reaction flask before starting the heating and stirring (1200 rpm) of reaction mixture. To estimate the conversion of phenol, 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. The rate of oxidation for the oxidation of phenol was determined by studying reactions at different temperatures and at constant molar ratios of substrate to H$_2$O$_2$, and catalyst. To test the stability of the polymer-anchored copper complexes and leaching of copper ion, the polymer-anchored copper ion complexes were recycled and reused in these reactions. To analyze the effect of the catalyst on the oxidation of, the reactions were also studied without catalysts.

RESULTS AND DISCUSSION

The oxidation of phenol with polymer-anchored HMBdMBn Schiff base complexes of copper ions was found to be higher and more selective than those with unsupported HMBdMBn Schiff base complex of copper(II) ion. These results clearly indicate that a polymer support plays a positive role in modifying the activity of copper-ion complexes, as reported in the literature [6]. 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.

3.1 Characterization of HMBdMBn Schiff base

The IR spectrum (Figure 1) of HMBdMBn Schiff base showed absorption bands at 1610 cm$^{-1}$ (>C =N), 1268 cm$^{-1}$ (<C =O) phenolic (Figure 1) and a broad band between 3350 and 2910 cm$^{-1}$ was also observed, which was assigned to phenolic OH. The elemental analysis of HMBdMBn Schiff base showed (wt%): C = 76.64, N = 8.06 and H = 5.79; Calcd (%): C = 77.07, N = 7.82 and H = 5.19, which corresponded to $C_{23}H_{22}N_2O_4$ empirical formula of HMBdMBn Schiff base.

The molecular weight of Schiff base was 357.37 g mol$^{-1}$ (Calcd 358.43 g mol$^{-1}$). The electronic spectra of HMBdMBn Schiff base showed absorption bands at 284 nm and 346 nm, which were assigned to π → π$^*$ and n → π$^*$ transitions. The $^1$H-NMR spectrum of the Schiff base showed signals at δ/ppm = 2.52(2H), 2.83(3H), 5.15(2H), 6.91(2H), 7.27(2H), 7.41(3H), 7.60(2H), and 8.66(2H) which corresponded to the structure of HMBdMBn Schiff base.

Scheme 1. Synthesis of HMBdMBn Schiff base

Figure 1. FTIR spectra of unsupported HMBdMBn Schiff base (A) & polymer supported HMBdMBn Schiff base (B).
3.2 Synthesis and characterization of A-HMBdMBn Schiff base and its anchoring on polymer beads

The elemental analysis of N, N’-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (A- HMBdMBn) Schiff base showed (wt%): C = 71.11, N = 13.00, and H = 7.02. The IR spectrum of A-HMBdMBn Schiff base showed absorption bands at low frequency (Figure 1B) in the IR spectrum of HMBdMBn Schiff base. The polymer-supported Schiff base showed new absorption bands at 1605 cm⁻¹ (C=O), 1266 cm⁻¹ (>C–O)phenolic, and 1538 cm⁻¹ for N-O group. The nitrosation of A-HMBdMBn Schiff base was confirmed by comparing the IR spectrum of HMBdMBn Schiff base with that of pure polymer beads. The decrease in intensity of absorption band at 1263 cm⁻¹ for >C–N group and new absorption bands appeared due to the formation of N–O group.

The elemental analysis of A- HMBdMBn Schiff base showed (wt%): C = 73.86, N = 13.45, and H = 6.22. The magnetic moment (µ) of A-HMBdMBn Schiff base was found to be 1.81 BM, which indicated that copper(II) ion was paramagnetic in nature with one unpaired electron. The magnetic moment (µ) and electronic configuration of copper(II) ion complex was paramagnetic in nature with one unpaired electron.

The complexation of copper(II) ion with HMBdMBn Schiff base showed significant variations in IR bands for >C–N and >C–O groups and new absorption bands appeared due to the formation of M–O and M–N bonds in copper complexes. (Figure 2) The disappearance of phenolic absorption band between 2910 and 3350 cm⁻¹ in the IR spectrum of HMBdMBn Schiff base after the complexation of copper ion was an evidence for the complexation of copper ion with HMBdMBn Schiff base. The polymer-supported Schiff base showed absorption bands at low frequency (Figure 1B) in comparison to free Schiff base (Figure 1A).

The anchoring of A-HMBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of HMBdMBn Schiff base anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1607 cm⁻¹ (>C=N), 1266 cm⁻¹ (>C–O)phenolic, and 1538 cm⁻¹ for N–O group. The nitrosation of HMBdMBn Schiff base on polymer beads (Figure 1). The appearance of new absorption bands and shift in characteristic absorption bands of HMBdMBn Schiff base after the complexation of copper ion was an evidence for anchoring of HMBdMBn Schiff base on polymer beads.

The complexation of copper(II) ion with HMBdMBn Schiff base showed variation in π→π* transition from 284 nm to 277 nm, and for the n→π* transition was changed from 346 nm to 307 nm (Table 1). The complexation of copper(II) ion with HMBdMBn Schiff base showed CT transition and δ→δ* transitions. These electronic transitions corresponded to t2g2e'2 configurations for copper(II) ion in this complex. The magnetic moment (µ) of Schiff base complexes of copper(II) ion was found to be 1.81 BM, which indicated that copper(II) ion complex was paramagnetic in nature with one unpaired electron. The magnetic moment (µ) and electronic configuration of copper(II) ion complex was confirmed by comparing the electronic spectra of copper complex and pure HMBdMBn Schiff base.

The complexation of copper(II) ion with HMBdMBn Schiff base showed new absorption band at 572 cm⁻¹ with free Schiff base and at 563 cm⁻¹ with polymer-anchored Schiff base, which was due to the formation of Cu–N bond between Cu(II) ion and Schiff base. The complexation of copper ion showed another new band due to the formation of bond between copper ion and phenolic oxygen (–O–Cu). The complexation of copper ion with Schiff base was further confirmed by comparing electronic spectra of copper complex and pure HMBdMBn Schiff base.

The complexation of copper(II) ion with HMBdMBn Schiff base showed variation in π→π* transition from 284 nm to 277 nm, and for the n→π* transition was changed from 346 nm to 307 nm (Table 1). The complexation of copper(II) ion with HMBdMBn Schiff base showed CT transition and δ→δ* transitions. These electronic transitions corresponded to t2g2e'2 configurations for copper(II) ion in this complex. The magnetic moment (µ) of Schiff base complexes of copper(II) ion was found to be 1.81 BM, which indicated that copper(II) ion complex was paramagnetic in nature with one unpaired electron. The magnetic moment (µ) and electronic configuration of copper(II) ion complex was confirmed by comparing the electronic spectra of copper complex and pure HMBdMBn Schiff base.
rations have suggested a square planar structure with dsp$^2$ hybridization for copper(II) ion complex.

**Table 1: Electronic transitions in unsupported and polymer supported copper ion complex of HMBdMBn Schiff base**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Frequencies $\lambda_{max}$/ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMBdMBn</td>
<td>284 284 346 346 346 346</td>
</tr>
<tr>
<td>P- HMBdMBn</td>
<td>281 281 341 341 341 341</td>
</tr>
<tr>
<td>HMBdMBn -Cu</td>
<td>277 277 307 307 354 354 561</td>
</tr>
<tr>
<td>P- HMBdMBn -Cu</td>
<td>271 271 301 301 349 349 557</td>
</tr>
</tbody>
</table>

3.4 Oxidation of phenol

The polymer support has facilitated the decomposition of intermediates; hence, per cent conversion of phenol was more with polymer-supported copper complex (Figure 3) in comparison to free copper complexes of HMBdMBn Schiff base (Table 3).

![FTIR spectra of polymer supported HMBdMBn-Cu complex](A) and polymer supported HMBdMBn Schiff base ligand (B)

**Scheme 6. Oxidation of phenol.**

The conversion of phenol by unsupported catalyst was initially high at 240 min and then after the conversion became almost constant due to substantial decrease in the concentration of oxidant and substrate in the reaction mixture (Table 2). Similar trends in substrate conversion were observed with supported catalysts at different time intervals as found with unsupported catalysts (Figure 3). The high activity of metal complexes on polymer support was due to the facile interactions of catalyst with substrate than with unsupported catalysts. The amount of phenol oxidized with hydrogen peroxide was almost equal to the sum of amount of catechol and hydroquinone produced, which discarded the formation of other reaction products such as polymeric phenols, but reaction showed high selectivity for catechol. The supported catalysts were recycled and also further evaluated for their catalytic activity after their applications in oxidation reactions. The efficiency of supported catalysts remained almost constant up to six recycles and then the efficiency decreased (Table 3). The product selectivity for catechol remained unaltered upon using recycled catalyst, which was an indication for the structural stability of copper complexes on polymer support as confirmed by comparing IR spectra of recycled catalyst with IR spectra of freshly prepared catalyst.

**Figure 3. Effect of reaction time on oxidation of phenol in presence of polymer-supported copper complexes.**

**Table 2. Catalytic activity of unsupported copper complexes (Cu-HMBdMBn) in oxidation of phenol (Ph).**

<table>
<thead>
<tr>
<th>Time/min</th>
<th>Cu-HMBdMBn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>4.7</td>
</tr>
<tr>
<td>30</td>
<td>10.0</td>
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<tr>
<td>45</td>
<td>18.1</td>
</tr>
<tr>
<td>60</td>
<td>23.9</td>
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<tr>
<td>90</td>
<td>28.3</td>
</tr>
<tr>
<td>240</td>
<td>30.0</td>
</tr>
<tr>
<td>720</td>
<td>30.6</td>
</tr>
<tr>
<td>1440</td>
<td>31.3</td>
</tr>
</tbody>
</table>

**Table 3. Efficiency of recycled supported catalysts (P-HMBdMBn -Cu) in oxidation of phenol.**

<table>
<thead>
<tr>
<th>Supported metal complexes</th>
<th>Recycle number</th>
<th>Conversion Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P- HMBdMBn -Cu</td>
<td>0  2  4  6  8</td>
<td>46.3 46.1 45.9 42.4 33.2</td>
</tr>
<tr>
<td>P- HMBdMBn -Cu</td>
<td>91.3 91.0 90.4 88.7 85.8</td>
<td></td>
</tr>
</tbody>
</table>

[Phenol]:[Catalyst]: [H$_2$O$_2$] = 1:1:1 (0.05M), Temp. = 70 °C, CH$_3$CN = 2.0 mL.

The rate of phenol conversion was high (1.57 x 10$^{-6}$ mole dm$^{-3}$ s$^{-1}$) in the presence of polymer-supported HMBdMBn Schiff base complexes of copper(II) than unsupported analogue (1.04 x 10$^{-6}$ mole dm$^{-3}$ s$^{-1}$).

3.5 Mechanism for oxidation of phenol

Considering the experimental findings for the oxidation of phenol with free and supported HMBdMBn Schiff base complexes of copper ion, the following reaction steps are proposed (Scheme 7). The free and polymer-supported Schiff base complexes of copper ion has produced active species (Cu-HMBdMBn-HOO) through fast interactions with hydrogen peroxide and HMBdMBn Schiff base. The active species was subsequently used in the formation of intermediates (Cu-HMBdMBn -Ph-HOO) through its interactions with phenol in a rapid equilibrium (K). The intermediate (Cu-HMBdMBn -Ph-HOO) has facilitated the nucleophilic attack of OOH species on ortho and para position on phenol to produce hydroxy-substituted phenols (Scheme 6). The reaction products, catalyst and hydroxyl ions were formed through decomposition of intermediates (Scheme 7 step 4) and finally the hydroxyl ions reacted with hydrogen ions, which were produced in step 1.
Scheme 7. Reaction steps of oxidation of phenol
1. INTRODUCTION
Schiff base complexes of transition-metal ions have shown significant catalytic activities in various reactions such as oxidation,[1] epoxidation of olefins,[2] polymerization of ethylenes,[3] etc. but supported metal-ion complexes have shown high catalytic activity[4-6] in comparison with unsupported catalysts. Cobalt(II) and manganese(II) ion complexes of salen on tailor-made polymer supports have shown considerable increases in activity due to a significant reduction in the mass transfer limitation for the reactants. Although metal ion complexes have been immobilized on various supports[7], their activity on polymer supports is quite high[8] because of the dynamic microenvironment[9] and liquid-phase conditions[10], in which an anchored catalyst is able to perform rotational and translational motions. The homogeneity of catalysts on zeolite[11] and silica[12] supports is significantly different from that on polymer supports.

The activity of polymer-supported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions in the oxidation of phenol[13-14] also showed variation with temperature, time, etc., which might be due to the change in concentration of substrate or catalyst. Although a number of polymer supported catalysts have been reported, the polymer anchored metal-ion complexes of the HMBdMBn Schiff base (N,N'-bis (4-amino-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base) have not been reported in the literature; hence, attempts have been made to synthesize and characterize polymer-supported Cu(II) complex of the HMBdMBn Schiff base for different industrial use.

2. EXPERIMENTAL
2.1 Materials
Divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai. The copper(II) chloride anhydrous was purchased from HiMedia Laboratories Pvt. Ltd, Mumbai. The 2-hydroxy-3-methylbenzaldehyde and 4-Methylbenzene-1,2-diamine were procured from Sigma-Aldrich, India. The 2-hydroxy-3-methylbenzylaldehyde (HMBdMBn) Schiff base was prepared by carrying out nitrosation and reduction reactions on HMBdMBn Schiff base and then reacting resulted A-HMBdMBn Schiff base with cross-linked chloromethylated polystyrene beads. The nitrosation of HMBdMBn Schiff base was carried out using 20.00 mmol (7.16 g) of HMBdMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at 5°C. The resulting N,N'-bis (4-nitrosso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-HMBdMBn) was filtered and washed with hot and cold water to remove reaction impurities. The reduction of NO-HMBdMBn was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of

2.2 Characterization of the HMBdMBn Schiff base and its copper(II) ion complex
IR spectra of HMBdMBn Schiff base and its copper complex were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of HMBdMBn Schiff base and its copper complex were recorded with Shimadzu 1601 PC UV-Vis Spectrophotometer by using sample null in a cuvette. Thermo gravimetric analysis (TGA) of HMBdMBn Schiff base and its copper(II) complex was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10°C/min. The loading of copper(II) ion on HMBdMBn Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_{max} of corresponding copper(II) ion. The 1H-NMR spectra of HMBdMBn Schiff base and its copper complex were recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (μ) of copper complex was measured using Vibrating Sample Magnetometer-155. The molecular weight of HMBdMBn Schiff base and its copper complex was determined using a Vapor Pressure Osmometer (Merk VAPRO 5600, Germany).

2.3 Synthesis of HMBdMBn and its copper complex
HMBdMBn Schiff base was synthesized by the modified procedure reported in the literature.[15] The reaction mixture containing 2-hydroxy-3-methylbenzaldehyde (20.00 mmol, 2.72g) and 4-Methylbenzene-1,2-diamine (10.00 mmol, 1.22g) in methanol was refluxed at 60°C for about 1 hr. The reaction mixture on cooling at low temperature produced light orange colored crystals, which were filtered and recrystallized with methanol. The copper complex of HMBdMBn Schiff base was prepared taking 100 ml methanolic solution of mixture of Schiff base (20.00 mmol, 7.16g) and 20.00 mmol of copper in a round bottom flask and refluxing at 60°C. After 8 h, the solution was cooled and copper complex was separated from the mother liquor. All reactions were performed under nitrogen atmosphere. Finally, copper complex was recrystallized in methanol and dried in a vacuum desiccator.

2.4 Synthesis of P-HMBdMBn Schiff base and its copper complex
To prepare polymer-anchored copper complex of HMBdMBn Schiff base, the N,N'-bis (4-amino-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (A-HMBdMBn) Schiff base was prepared by carrying out nitrosation and reduction reactions on HMBdMBn Schiff base and then reacting resulted A-HMBdMBn Schiff base with cross-linked chloromethylated polystyrene beads. The nitrosation of HMBdMBn Schiff base was carried out using 20.00 mmol (7.16 g) of HMBdMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at 5°C. The resultant N,N'-bis (4-nitrosso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-HMBdMBn) was filtered and washed with hot and cold water to remove reaction impurities. The reduction of NO-HMBdMBn was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of
metallic iron, which produced A-HMBdMBn Schiff base. To immobilize the prepared A-HMBdMBn Schiff base on cross-linked chloromethylated polystyrene, the methanol swollen polymer beads (5.0 g) were refluxed in 50 ml methanol containing 20.00 mmol (7.76 g) A-HMBdMBn Schiff base. After 8 h, the HMBdMBn Schiff base-anchored polymer beads were separated and dried in a vacuum desiccator. The amount of HMBdMBn Schiff base loaded on polymer beads was estimated with elemental analysis. Subsequently, the copper ion was loaded by keeping HMBdMBn loaded polymer beads (5.0 g) for 10 h in an aqueous solution (50 ml) of copper ion (20.00 mmol). Finally, the polymer beads were separated and dried at 70ºC in a vacuum oven after washing with hot and cold water. The loading of copper ion on polymer beads was determined by analyzing the loading solution with an Atomic Absorption Spectrometer. The amount of copper ion on free and polymer-supported HMBdMBn Schiff base was calculated as complexation of copper ion using the amount of copper ion loaded on polymer beads.

\[
\text{Amount of copper ion loaded} = \frac{\text{Amount of Schiff base used for loading}}{X \times 100}
\]

### Table 1: FTIR and UV data for HMBdMBn Schiff base and its copper complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Absorption frequencies / cm(^{-1})</th>
<th>Frequencies (\lambda_{\text{max}}) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(u_{C=N})</td>
<td>(u_{C-O})</td>
</tr>
<tr>
<td>HMBdMBn</td>
<td>1610</td>
<td>1268</td>
</tr>
<tr>
<td>P-HMBdMBn</td>
<td>1602</td>
<td>1260</td>
</tr>
<tr>
<td>HMBdMBn-Cu</td>
<td>1597</td>
<td>1316</td>
</tr>
<tr>
<td>P-HMBdMBn-Cu</td>
<td>1592</td>
<td>1310</td>
</tr>
</tbody>
</table>

The molecular weight of Schiff base was 357.37 g mol\(^{-1}\) (Calcd 358.43 g mol\(^{-1}\)). The electronic spectra of HMBdMBn Schiff base showed absorption bands at 284 nm and 346 nm, which were assigned to \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions. The 1H-NMR spectrum of the Schiff base showed signals at \(\delta/pmm = 2.52(6H), 2.83(3H), 5.15(2H), 6.91(2H), 7.27(2H), 7.41(3H), 7.60(2H),\) and 8.66(2H) which corresponded to the structure of HMBdMBn Schiff base.

The TGA of P-HMBdMBn Schiff base showed a weight loss of 40.4 wt% at 500°C, but its copper(II) ion complex showed a weight loss of 33.0 wt%, at same temperature. (Figure 1) In addition to thermal analysis, the free and polymer-supported copper complex of HMBdMBn Schiff base were also characterized by NMR, IR and UV techniques to provide a proof for the complexation of copper ion.

![Figure 1](image1.png)

**Figure 1.** Thermal stability of the polymer-supported HMBdMBn Schiff base and its copper complex.

### 3. RESULTS AND DISCUSSION

The polymer support plays a positive role in modifying the activity of metal-ion complexes, as reported in the literature [6]. 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. Although the amount of loaded metal ions 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 [13-14].

#### 3.1 Characterization of HMBdMBn Schiff base

The HMBdMBn Schiff base was obtained by refluxing 2-hydroxy-3-methylbenzaldehyde and 4-Methylbenzene-1,2-diamine with a substantial yield (86.2 wt%) (Scheme 1). The IR spectrum of HMBdMBn Schiff base showed absorption bands at 1610 cm\(^{-1}\) (\(>\text{C}=\text{N}\)), 1268 cm\(^{-1}\) (\(\text{C}=\text{O}\)) phenolic and a broad band between 3350 and 2910 cm\(^{-1}\) for phenolic OH. (Table 1) The elemental analysis of HMBdMBn Schiff base showed (wt%): C = 76.64, N = 8.06 and H = 5.79; Calcd (%): C = 77.07, N = 7.82 and H = 6.19, which corresponded to the empirical formula \(C_{23}H_{12}N_{2}O_2\).

#### 3.2 Synthesis and characterization of Amino-HMBdMBn Schiff base and its anchoring on polymer beads

The nitrosation of HMBdMBn Schiff base was carried out in the presence of NaNO\(_2\)/HCl, which gave 86.5% yield of \(N, N'\)-bis(4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (Scheme 2). The elemental analysis showed (wt%): C = 67.00, N = 12.63, and H = 5.00; Calcd (wt%): C = 66.34, N = 13.45, and H = 4.84, which corresponded to \(C_{23}H_{12}N_{2}O_2\) formula of NO-HMBdMBn. The molecular weight
of NO-HMBdMBn was 415.03 g mol$^{-1}$ (Calcd 416.43 g mol$^{-1}$). The IR spectrum of NO-HMBdMBn showed absorption bands at 1607 cm$^{-1}$ (C=O), 1613 cm$^{-1}$ (C=C =N) and 1620 cm$^{-1}$ for N=N group. The nitration of HMBdMBn Schiff base showed a shift in NMR signals in comparison to NMR signals observed with pure HMBdMBn Schiff base. The nitrosated HMBdMBn Schiff base showed proton signals at $\delta$/ppm = 2.54(6H), 2.88(3H), 5.15(2H), 7.35(2H), 7.42(3H), 7.96(2H), and 8.69(2H), which corresponded to the structure of nitrosated HMBdMBn Schiff base. The protons ortho to nitro group in HMBdMBn Schiff base were deshielded; hence, their signals appeared at 7.35 and 7.96 ppm in place of 7.27 and 7.69 ppm respectively of pure HMBdMBn Schiff base. The proton signal at 6.91 ppm was missing due to the substitution of nitro group in the benzene. The NO-HMBdMBn was reduced with iron(III) ions in the presence of hydrochloric acid, which gave 81.3 wt% yield of A-HMBdMBn Schiff base. The elemental analysis of A-HMBdMBn Schiff base showed (wt%); C = 70.54, N = 13.00, and H = 7.02, Calcd (wt%): C = 71.11, N = 14.42, and H = 6.23, which corresponded to C$_6$H$_2$(NO)$_2$ empirical formula. The molecular weight of A-HMBdMBn Schiff base was found to be 387.23 g mol$^{-1}$ (Calcd 388.46 g mol$^{-1}$). The IR spectrum of A-HMBdMBn Schiff base showed absorption bands at 1605 cm$^{-1}$ (C=N), 1263 cm$^{-1}$ (C=O)phenolic, and a band between 1632 and 1618 cm$^{-1}$ for C=N group. The $^1$H-NMR spectrum of A-HMBdMBn Schiff base showed proton signals at $\delta$/ppm = 2.52(6H), 2.85(3H), 4.15 (4H), 5.15(2H), 6.36 (2H), 7.42(3H), 6.81(2H), and 8.69(2H), which corresponded to the structure of A-HMBdMBn Schiff base.

The synthesized Schiff base was anchored on cross-linked chloromethylated polystyrene beads by refluxing A-HMBdMBn Schiff base with polymer beads in DMF for 8 h at 60°C. The anchoring of A-HMBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of HMBdMBn Schiff base anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1602 cm$^{-1}$ (C=N), 1260 cm$^{-1}$ (C=O)phenolic, and a band between 1629 and 1618 cm$^{-1}$ for C=N group. The $^1$H-NMR spectrum of A-HMBdMBn Schiff base showed proton signals at $\delta$/ppm = 2.52(6H), 2.85(3H), 4.15 (4H), 5.15(2H), 6.36 (2H), 7.42(3H), 6.81(2H), and 8.69(2H), which corresponded to the structure of A-HMBdMBn Schiff base.

### 3.3 Characterization of free and polymer-anchored copper complex of HMBdMBn Schiff base

The loading of copper ion on free and polymer-supported HMBdMBn Schiff base was carried out by refluxing free Schiff base and polymer-anchored Schiff base in copper chloride solution at 60°C for 6 h (Scheme 1). The copper complex of free Schiff base (HMBdMBn-Cu) and polymer-anchored Schiff base (P-HMBdMBn-Cu) after separation and purification were analyzed for their structures and loading of copper ion. The complexation of copper(II) ions on free HMBdMBn Schiff base and polymer-anchored Schiff base in copper chloride solution was confirmed by comparing the IR spectrum of HMBdMBn Schiff base anchored polymer beads with spectroscopy of pure polymer beads. The amount of A-HMBdMBn Schiff base anchored on polymer beads was 87.0 wt% (Scheme 1).

The complexation of copper(II) ion showed new absorption band at 572 cm$^{-1}$ with free Schiff base and at 563 cm$^{-1}$ with polymer-anchored Schiff base, which was due to the formation of Cu–N bond. And also another due to the formation of bond between copper ion and phenolic oxygen (O=Cu). (Table 1)

The complexation of copper(II) ion with HMBdMBn Schiff base showed variation in transition from 284 nm to 277 nm, and for the n→π* transition was changed from 346 nm to 307 nm (Table 1). The complexation of copper(II) ion with HMBdMBn Schiff base showed CT transition and d→d transitions. These electronic transitions corresponded to $t_{2g}$ → e$^1$ configurations. The magnetic moment(µ) of Schiff base complexes of copper(II) ion was found to be 1.81BM, which indicated that copper(II) ion complex was paramagnetic in nature with one unpaired electron. The magnetic moment ($\mu$) and electronic configurations have suggested a square planar structure with dsp$^3$ hybridization for copper(II) complex.

### 4. CONCLUSIONS

Polymer-supported copper-ion complex of the HMBdMBn Schiff base was synthesized and characterized for their structures. The experimental results showed that copper complex of HMBdMBn Schiff base is square planar geometry. And the polymer supported complex is more stable than unsupported analogue.

### Acknowledgments

The authors are also thankful to Indian Academy of Sciences, India, IISER Kolkata, Ravenshaw University, KIIT University and National Institute of Technology, Raipur for providing research opportunity.

### Reference

Synthesis and structural studies of nickel complex supported by-ONNO-tetra dentate Schiff-base ligand: efficient catalysts for oxidation of phenol

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Abstract: The free and polymer anchored complex of nickel [3-MHBdMBn-Ni and P-3-MHBdMBn-Ni], supported by -ONNO-tetradentate Schiff-base ligand are prepared by the reactions of nickel solution with one molar equivalent of unsupported 3-MHBdMBn (N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine) or polymer supported (P-3-MHBdMBn) Schiff-base ligands in methanol. The structural study reveal that nickel (II) complex of 3-MHBdMBn Schiff base is square planar in geometry. Complexation of nickel ion increased the thermal stability of 3-MHBdMBn Schiff base. The catalytic activity of nickel complex towards the oxidation of phenol is investigated in the presence of hydrogen peroxide. Experimental results indicate that the reactivity of P-3-MHBdMBn-Ni is dramatically affected by the polymer support over 3-MHBdMBn-Ni and the rate of oxidation (Rp) for unsupported one is 1.28 x 10^-6 mole dm^-3 s^-1 and for supported analogue is 1.99 x 10^-6 mole dm^-3 s^-1.

Keywords: Schiff Base, Polymer Support, Catalysis, Nickel, Phenol, Oxidation

1. Introduction

Various metal ions and their complexes have been used widely in homogeneous catalyzed reactions but inherent disadvantages associated with homogeneous catalysis were minimized by using supported metal complexes, which sometime have shown high catalytic activities in comparison to unsupported analogues. The supported catalysts are easily recovered without any substantial loss in their catalytic activity [1-2] but homogeneous catalysts are not recovered easily. The Schiff base complexes of transition metal ions shown high catalytic activities in various chemical reactions such as epoxidation of olefins,[3] oxidation,[4-5] and polymerization of ethylene,[6-7] but polymer-supported metal complexes showed high catalytic activity [4,5,8-10], in comparison to homogeneous catalysts. The manganese(II) salen complexes anchored on tailor-made polymers were more enantioselective without any mass transfer limitation for alkenes on polymer supports.[11] The transition metal complexes were also anchored on other supports,[12-15] and have been used in selective oxidation of phenols but oxidation of phenol using metal salen complexes on polymer supports found to be more efficient and selective in comparison to homogeneous systems, as the polymeric supports provided better control on efficiency of catalysts [8] due to microenvironment provided by polymer chains for the substrates in comparison to zeolites [16] and silica.[17] The metal complexes on solid supports are immobilized either physically or by forming a covalent bond between metal complexes and supports.[8] But the recovery of physically linked catalysts has been found to be low in comparison to covalently bound catalysts due to the leaching of catalysts. The oxidation of phenol using unsupported Schiff base complexes of metal ions is reported,[18] but the oxidation of phenol using polymer-supported transition metal complexes was found to be high [19] in the presence of tert-butyl hydroperoxide (t-BHP). In these investigations, the homogeneous cobalt salen complexes have shown poor
catalytic activity in comparison to polymer bound cobalt (II) salen complexes. On doubling the concentration of polymer bound catalyst, the conversion of phenol was doubled, whereas in case of homogeneous conditions, the phenol conversion was increased to 1.7-fold. The activity of metal complexes on polymer supports has normally found to be more in comparison to metal complexes on inorganic supports [20-22]. The polymer-supported Schiff base complexes of metal ions also showed variations in the decomposition of hydrogen peroxide with their redox potentials, [20] which provided a useful criterion to explain the activity of metal ions in the oxidation of phenol in the presence of hydrogen peroxide as the oxidant. The activity of polymer-supported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions in the oxidation of phenol [21-22] also showed variation with temperature, time, etc, which might be due to the change in concentration of substrate or catalyst. The oxidation of phenol in the presence of metal complexes of salen and hydrogen peroxide as the oxidant is reported, but catalytic activity of metal complexes of N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MHBdMBn) Schiff base is not reported in the literature; hence, in these investigations an attempt has been made to prepare polymer-supported nickel complex of 3-MHBdMBn Schiff base and to characterize them for their structures and catalytic activity in the oxidation of phenol in the presence of hydrogen peroxide as an oxidant.

2. Experimental

2.1. Materials

Divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai, India and used to anchor synthesized 3-MHBdMBn Schiff base complexes of metal ions. The anhydrous chloro salts of nickel (II) ions were purchased from Ranbaxy, Mumbai, India and used without further purifications. The phenol, hydrogen peroxide (30.0 wt %), 2-hydroxy-3-methylbenzaldehyde (3-MHBd) and 4-Methylbenzene-1,2-diamine (MBn) were procured from E. Merck, India. Other chemicals and solvents were of analytical grade (>99.0 wt %) and used after purifications with standard methods. [23]

2.2. Characterization of 3-MHbdMBn Schiff Base and Its Metal Complexes

IR spectra of 3-MHBdMBn Schiff base and its nickel complex were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of 3-MHBdMBn Schiff base and its nickel complex were recorded with Shimadzu 1601 PC UV–Vis Spectrophotometer by using sample mull in a cuvette. Thermogravimetric analysis (TGA) of 3-MHBdMBn Schiff base and its nickel complex was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 5⁰C min⁻¹. The loading of metal ions on 3-MHBdMBn Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ max of nickel ions. The amount of 3-MHBdMBn Schiff base anchored on polymer beads and its composition were estimated using Haraes Carlo Ebra 1108 Elemental Analyzer. The 'H-NMR spectra of 3-MHBdMBn Schiff base and nickel complex were recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d⁶ as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (µ) of nickel complex was measured using Vibrating Sample Magnetometer-155. The molecular weight of 3-MHBdMBn Schiff base and its nickel complex was determined using a Vapor Pressure Osmometer (Merk VAPRO 5600, Germany).

2.3. Synthesis of N, N'-Bis (2-Hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1,2-Diamine Schiff Base (3-MHbdMBn) and Its Metal Complexes

The 3-MHBdMBn Schiff base was synthesized modifying the procedure reported in the literature,[21] The reaction mixture containing 2-hydroxy-3-methylbenzaldehyde (20.00 mmol, 2.72 g) and 4-Methylbenzene-1,2-diamine (10.00 mmol, 1.22 g) in methanol was refluxed at 60°C for about 1 hr. The reaction mixture on cooling at low temperature produced light orange colored crystals, which were filtered and recrystallized with methanol. The metal complexes of 3-MHBdMBn Schiff base were prepared taking 100 ml methanolic solution of mixture of Schiff base (20.00 mmol, 7.16 g) and 20.00 mmol of metal ions in a round bottom flask and refluxing at 60°C. After 8 h, the solution was cooled and crystalline metal complexes were separated from the mother liquor. Finally, metal complexes were recrystallized in methanol and dried in a vacuum desiccator.

2.4. Synthesis of Polymer-Anchored N, N'-Bis (2-Hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1,2-Diamine Schiff Base and Its Nickel Complex

To prepare polymer-anchored nickel complex of 3-MHBdMBn Schiff base, the N, N'-bis (4-amino-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (A-3-MHBdMBn) Schiff base was prepared by carrying out nitrosation and reduction reactions on 3-MHBdMBn Schiff base and then reacting resulted A-3-MHBdMBn Schiff base with cross-linked chloromethylated polystyrene beads. The nitrosation of 3-MHBdMBn Schiff base was carried out using 20.00 mmol (7.16 g) of 3-MHBdMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at -5°C. The resultant N, N'-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-3-MHBdMBn) was filtered and washed
with hot and cold water to remove reaction impurities. The reduction of NO-3-MHBdMBn was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of metallic iron, which produced A-3-MHBdMBn Schiff base. To immobilize the prepared A-3-MHBdMBn Schiff base on cross-linked chloromethylated polystyrene, the methanol swollen polymer beads (5.0 g) were refluxed in 50 ml methanol containing 20.00 mmol (7.76 g) A-3-MHBdMBn Schiff base. After 8 h, the 3-MHBdMBn Schiff base-anchored polymer beads were separated and dried in a vacuum desiccator. The amount of 3-MHBdMBn Schiff base loaded on polymer beads was estimated with elemental analysis. Subsequently, the metal ions were loaded by keeping 3-MHBdMBn loaded polymer beads (5.0 g) for 10 h in an aqueous solution (50 ml) of metal ions (20.00 mmol). 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 nickel ion on polymer bead was determined by analyzing the loading solution with an Atomic Absorption Spectrometer. The loading of nickel ion on free and polymer-supported 3-MHBdMBn Schiff base was calculated as complexation of nickel ion using the amount of 3-MHBdMBn Schiff base taken initially and the amount of nickel ion loaded on polymer beads.

\[
\text{Complexation of metal ions} = \frac{\text{Amount of nickel ion loaded}}{\text{Amount of Schiff base used for loading}} \times 100
\]

2.5. Catalytic Activity of Metal Complexes in Oxidation of Phenol

To evaluate the catalytic activity of free and polymer-supported nickel complex of 3-MHBdMBn Schiff base, the oxidation of phenol was carried out using hydrogen peroxide as the oxidant at fixed ionic strength (0.10 M) and hydrogen ions concentration (pH 7.0) in the 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 0.05 M phenol (4.70 g). The oxidation of phenol was carried out adding 5.67 g (0.05 M) hydrogen peroxide (30.0 wt %) in the reaction mixture and 2.0 ml chlorobenzene as an internal standard. The water condenser and supply of nitrogen were attached with reaction flask before starting the heating and stirring (1200 rpm) of reaction mixture. Gas chromatography was used to follow these reactions at different time intervals. The retention time of standards was used to identify the reaction products, and product selectivity was measured using peak areas of reaction products in the chromatograms. The reactions were also studied without using catalysts to analyze the effect of catalyst in the oxidation of phenol.

3. Results and Discussion

Investigations have revealed that polymer-supported metal complexes are sometimes more catalytic and efficient than free and unsupported analogs. [19-20] the activity of catalysts also showed dependence on properties of polymer supports and amount of loaded catalysts. Thermal stability of catalysts is required to be high, if these catalysts have to be applied in high temperature reactions. Therefore, thermal analysis of supported metal complexes was carried out to evaluate their possible applications in high temperature reactions and to provide a proof for complexation of metal ions with polymer-anchored 3-MHBdMBn Schiff base. The TGA of polymer supported 3-MHBdMBn Schiff base showed a weight loss of 40.4 wt% at 500°C, but its nickel(II) ion complex showed a weight loss of 36.5 wt% at same temperature, which was clear indication that nickel(II) ion complex was more stable than Schiff base (Figure 1).

![Figure 1. Thermal stability of polymer-supported 3-MHBdMBn Schiff base and its nickel complex](image)

In addition to thermal analysis, the free and polymer-supported nickel complex of 3-MHBdMBn Schiff base was also characterized by IR and UV techniques to provide a proof for the complexation of metal ions and to decide the structures and geometry of complex on the basis of elemental analysis and magnetic properties.

3.1. Characterization Of N, N'-Bis (2-Hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1, 2-Diamine (3-Mhbdmbn) Schiff Base

The 3-MHBdMBn Schiff base was obtained by refluxing 2-hydroxy-3-methylbenzaldehyde (3-MHbd) and 4-Methylbenzene-1, 2-diamine (MBn) for 1hr at 60°C in methanol, which produced a substantial yield (86.2 wt %) of 3-MHBdMBn Schiff base (Scheme 1). The IR spectrum (Figure 2) of 3-MHBdMBn Schiff base showed absorption
bands at 1610 cm\(^{-1}\) (\(>\text{C} = \text{N}\)), 1268 cm\(^{-1}\) (\(>\text{C}–\text{O}\)) phenolic (Figure 2A) and a broad band between 3350 and 2910 cm\(^{-1}\) was also observed, which was assigned to phenolic OH. The elemental analysis of 3-MHBDMbn Schiff base showed (wt %): C = 76.64, N = 8.06 and H = 5.79; Calcd (%): C = 77.07, N = 7.82 and H = 6.19, which corresponded to C23H22N2O2 empirical formula of 3-MHBDMbn Schiff base.

The molecular weight of Schiff base was 357.37 g mol\(^{-1}\) (Calcd 358.43 g mol\(^{-1}\)). The electronic spectra of 3-MHBDMbn Schiff base (Figure 3) showed absorption bands at 284 nm and 346 nm, which were assigned to \(\pi \rightarrow \pi^*\) and \(n \rightarrow \pi^*\) transitions. The 1H-NMR spectrum of HPPn Schiff base showed signals at \(\delta/\text{ppm} = 2.52(6\text{H}), 2.83(3\text{H}), 5.15(2\text{H}), 6.91(2\text{H}), 7.27(2\text{H}), 7.41(3\text{H}), 7.60(2\text{H}), \) and 8.66(2H) which corresponded to the structure of 3-MHBDMbn Schiff base as shown in Scheme 1.

Figure 2. FTIR spectra of unsupported 3-MHBDMbn Schiff base (A) and polymer supported 3-MHBDMbn Schiff base (B)

Figure 3. Electronic spectra of unsupported and polymer supported 3-MHBDMbn Schiff base

3.2. Synthesis and Characterization Of N, N'-Bis (4-Amino-2-Hydroxy-3-Methylbenzaldehyde) 4-Methylbenzene-1, 2-Diamine (A-3-MHBdMbn) Schiff Base And Its Anchoring On Polymer Beads

The nitrosation of 3-MHBDMbn Schiff base was carried out in the presence of NaNO\(_2\)/HCl, which gave 86.5% yield of N, N'-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-3-MHBdMbn) (Scheme 2). The elemental analysis of N, N'-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine showed (wt %): C = 67.00, N = 12.63, and H = 5.00; Calcd (wt %): C = 66.34, N = 13.45, and H = 4.84, which corresponded to C\(_{23}\)H\(_{20}\)N\(_4\)O\(_4\) formula of nitrosated Schiff base. The molecular weight of NO-3-MHBDMbn was 415.03 g mol\(^{-1}\) (Calcd 416.43 g mol\(^{-1}\)). The IR spectrum of NO-3-MHBDMbn showed absorption bands at 1607 cm\(^{-1}\) (\(>\text{C} = \text{N}\)), 1266 cm\(^{-1}\) (\(>\text{C}–\text{O}\)) phenolic, and 1530 cm\(^{-1}\) and 1320 cm\(^{-1}\) for N–O group. The nitrosation of 3-MHBDMbn Schiff base showed a shift in NMR signals in comparison to NMR signals observed with pure 3-MHBDMbn Schiff base. The nitrosated 3-MHBDMbn Schiff base showed proton signals at \(\delta/\text{ppm} = 2.54(6\text{H}), 2.88(3\text{H}), 5.15(2\text{H}), 7.35(2\text{H}), 7.42(3\text{H}), 7.96(2\text{H}), \) and 8.69(2H), which corresponded to the structure of nitrosated 3-MHBDMbn Schiff base as shown in Scheme 2. The protons ortho to nitroso group in 3-MHBDMbn Schiff base were deshielded; hence, their signals appeared at 7.35 and 7.96 ppm in place of 7.27 and 7.60 ppm respectively, of pure 3-MHBDMbn Schiff base. The proton signal at 6.91 ppm was missing due to the substitution of nitroso group in the benzene. The NO-3-MHBDMbn was reduced with iron (III) ions in the presence of hydrochloric acid, which gave 81.3 wt% yield of A-3-MHBDMbn Schiff base as shown in Scheme 2. The A-3-MHBDMbn Schiff base was characterized. The elemental analysis of A-3-MHBDMbn Schiff base showed (wt%): C = 70.54, N = 13.00, and H = 7.02, Calcd (wt%): C

Scheme 1. N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (3-MHBDMbn) Schiff base
The synthesized A-3-MHBdMBn Schiff base was anchored on cross-linked chloromethylated polystyrene beads by refluxing A-3-MHBdMBn Schiff base with polymer beads in DMF for 8 h at 60°C. The amount of A-3-MHBdMBn Schiff base anchored on polymer beads was 87.0 wt% (Scheme 3). The anchoring of A-3-MHBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of 3-MHBdMBn Schiff base anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1602 cm⁻¹ (>C=N), 1260 cm⁻¹ (>C–O) phenolic, and a broadband between 1629 and 1610 cm⁻¹ (>C=N), which were absent in the IR spectrum of pure polymer beads, but were present in free Schiff base. The IR spectrum of pure polymer beads showed absorption band at 1262 cm⁻¹, which is attributed to C–Cl bond of chloromethyl in cross-linked polymer beads. The decrease in the intensity of absorption band at 1262 cm⁻¹ in polymer-anchored 3-MHBdMBn Schiff base than pure polymer beads was an evidence for anchoring of 3-MHBdMBn Schiff base on polymer beads. The appearance of new absorption bands and shift in characteristic absorption bands of 3-MHBdMBn Schiff base were also used as evidence for anchoring of 3-MHBdMBn Schiff base on polymer beads.

3.3. Characterization of Free and Polymer-Anchored Metal Complexes of 3-MHbdmbn Schiff Base

The loading of nickel ion on free and polymer-supported 3-MHBdMBn Schiff base was carried out by refluxing free Schiff base (Scheme 4) and polymer-anchored Schiff base in solution of metal salt at 60°C for 6 h (Scheme 5). The metal complexes of free Schiff base (3-MHBdMBn-Ni) and polymer-anchored Schiff base (P-3-MHBdMBn-Ni) after separation and purification were analyzed for their structures and loading of nickel ion. The complexation of nickel(II) ion on free 3-MHBdMBn Schiff base and polymer-anchored Schiff base was 85.62 and 86.88 wt% respectively (Table 1). These results have clearly suggested that the loading of nickel ion on polymer-supported 3-MHBdMBn Schiff base was higher than free 3-MHBdMBn Schiff base.

Table 1. Efficiency of complexation (EC) of nickel ion (wt %)

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>Complexation (EC) of nickel(II) ion (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported 3-MHBdMBn Schiff base</td>
<td>85.62</td>
</tr>
<tr>
<td>Polymer supported 3-MHBdMBn Schiff base</td>
<td>86.88</td>
</tr>
</tbody>
</table>

[3-MHBdMBn] = 20 mmol, [Nickel ion] = 20 mmol
The complexation of nickel ion with 3-MHBdMBn Schiff base showed significant variations in IR 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 complex. The disappearance of phenolic absorption band between 2910 and 3350 cm\(^{-1}\) in the IR spectrum of 3-MHBdMBn Schiff base after the complexation of nickel ion was an evidence for the complexation of metal ions with 3-MHBdMBn Schiff base. The polymer-supported Schiff base showed absorption bands at low frequency (Figure 2B) in comparison to free Schiff base (Figure 2A). On complexation with nickel(II) ion, the frequency of >C=N absorption band of free Schiff base has decreased from 1610 to 1598 cm\(^{-1}\), whereas polymer-supported Schiff base showed variation from 1602 to 1594 cm\(^{-1}\) (Figure 4).

These variations in IR band corresponding to >C=N group of 3-MHBdMBn Schiff base were used as evidence for interactions of metal ions with azomethine nitrogen (>C=N) of 3-MHBdMBn Schiff base. The complexation of nickel(II) ions showed new absorption band at 424 cm\(^{-1}\) with free Schiff base and at 420 cm\(^{-1}\) with polymer-anchored Schiff base, which was due to the formation of M–N bond between nickel(II) ion and Schiff base. The complexation of nickel(II) ion showed another new band due to the formation of bond between nickel and phenolic oxygen (–O–M) with polymer-supported 3-MHBdMBn Schiff base at 525 cm\(^{-1}\) (Figure 4).

The complexation of metal ions with Schiff base was further confirmed by comparing electronic spectra of nickel complex and pure 3-MHBdMBn Schiff base. The complexation of nickel(II) ion with 3-MHBdMBn Schiff base showed variation in π → π\(^*\) transition from 284 nm to 273 nm and (Table 2) the n → π\(^*\) transition of 3-MHBdMBn Schiff base was changed from 346 nm to 295 nm. The charge transfer (CT) and d → d transitions were also used as evidence for complexation of nickel with Schiff base. These electronic transitions corresponded to t_{2g}\(^6\) e_{g}\(^2\) configurations for nickel(II) ion in this complex.

**Table 2.** Electronic transitions in unsupported and polymer supported nickel complex of 3-MHBdMBn Schiff base

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Frequencies λ(_{max}) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>π→π(^*)</td>
</tr>
<tr>
<td>3-MHBdMBn</td>
<td>284</td>
</tr>
<tr>
<td>P-3-MHBdMBn</td>
<td>281</td>
</tr>
<tr>
<td>3-MHBdMBn-Ni</td>
<td>273</td>
</tr>
<tr>
<td>P-3-MHBdMBn-Ni</td>
<td>268</td>
</tr>
</tbody>
</table>
The magnetic moment (µ) of nickel Schiff base complex was found to be 0.93BM, which indicated that nickel(II) ion complex was diamagnetic in nature with zero unpaired electron. The magnetic moment (µ) and electronic configurations have suggested a square planar structure with dsp² hybridization for nickel complex (Scheme 6).

### 3.4. Oxidation of Phenol

The catalytic activity of free and polymer-supported nickel complex of 3-MHBdMBn Schiff base was evaluated by studying the oxidation of phenol in the presence of hydrogen peroxide. The gas chromatographic analysis was used to determine the product selectivity and to estimate the percent conversion of phenol. The catechol (CTL) was a major reaction product in the oxidation of phenol (Scheme 7). The formation of reaction products was attributed to enzymatic behaviour of metal complexes of 3-MHBdMBn Schiff base.

![Scheme 7. Oxidation of Phenol](image)

The polymer support has facilitated the decomposition of these intermediates; hence, per cent conversion of phenol was more with polymer-supported nickel complex (Figure 5) in comparison to free complex of 3-MHBdMBn Schiff base (Table 3). The conversion of phenol was initially high at 240 min and then after the conversion became almost constant due to substantial decrease in the concentration of oxidant and substrate in the reaction mixture (Table 3). Similar trends in substrate conversion were observed with supported catalysts at different time intervals as found with unsupported catalysts (Figure 5 & Table 3). The oxidation reaction also showed dependence on type of catalyst. The high activity of metal complexes on polymer support was due to the facile interactions of catalyst with substrate than 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 sum of amount of CTL and hydroquinone (HQ) produced, which discarded the formation of other reaction products such as polymeric phenols.

The amount of CTL and HQ was equal to phenol conversion, but reaction showed high selectivity for CTL. The supported catalysts were recycled and also further evaluated for their catalytic activity after their applications in oxidation reactions. The efficiency of supported catalysts remained almost constant up to six recycles and then the efficiency decreased (Table 4). The product selectivity for CTL remained unaffected on using recycled catalysts, which was an indication for the structural stability of metal complexes on polymer support as confirmed by comparing IR spectra of recycled catalysts with IR spectra of freshly prepared catalysts. The activity of metal complexes in substrate conversion and product selectivity was evaluated at different molar ratios of substrate to hydrogen peroxide and catalyst.

![Figure 5. Effect of reaction time on oxidation of phenol in presence of polymer-supported and unsupported nickel complexes](image)

**Table 3. Catalytic activity of unsupported and polymer supported nickel complex (Ni-3-MHBdMBn) in oxidation of phenol (Ph).**

<table>
<thead>
<tr>
<th>Time/min</th>
<th>P-3-MHBdMBn-Ni</th>
<th>3-MHBdMBn-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>12.6</td>
<td>4.8</td>
</tr>
<tr>
<td>30</td>
<td>32.4</td>
<td>11.2</td>
</tr>
<tr>
<td>45</td>
<td>39.6</td>
<td>19.1</td>
</tr>
<tr>
<td>60</td>
<td>43</td>
<td>23.5</td>
</tr>
<tr>
<td>90</td>
<td>55.4</td>
<td>33.3</td>
</tr>
<tr>
<td>240</td>
<td>57.5</td>
<td>37</td>
</tr>
<tr>
<td>720</td>
<td>58.6</td>
<td>38.1</td>
</tr>
<tr>
<td>1440</td>
<td>60.1</td>
<td>39</td>
</tr>
</tbody>
</table>

**Table 4. Efficiency of recycled supported catalysts (P-3-MHBdMBn-M) in oxidation of phenol.**

<table>
<thead>
<tr>
<th>Supported metal complexes</th>
<th>Recycle number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>P-3-MHBdMBn-Ni</td>
<td></td>
</tr>
<tr>
<td>Conversion Selectivity</td>
<td>94.1</td>
</tr>
</tbody>
</table>

[Phenol]: [Catalyst]: [H₂O₂] = 1:1:1 (0.05M), Temp. = 70°C. CH₃CN = 2.0 mL.
The rate of phenol conversion was high (1.99 x 10^6 mole dm\(^{-3}\) s\(^{-1}\)) in the presence of polymer-supported 3-MHBdMBn Schiff base complexes of nickel(II) ion than unsupported Schiff base analogue (1.28 x 10^6 mole dm\(^{-3}\) s\(^{-1}\)) (Table 5). The turnover number (TON) for the oxidation of phenol was high (13.51 g mol\(^{-1}\)Ni hr\(^{-1}\)) in the presence of polymer supported Schiff base complex in comparison to unsupported Schiff base complex (8.69 g mol\(^{-1}\)Ni hr\(^{-1}\)) at a molar ratio of 1:1 of H\(_2\)O\(_2\) to phenol and catalyst (Table 5). The rate of substrate conversion and TON in the oxidation of phenol varied significantly with molar ratio of hydrogen peroxide but product selectivity in both cases remained almost constant (Tables 5).

Table 5. Oxidation of phenol by nickel complex of 3-MHBdMBn Schiff base: Phenol conversion, selectivity for catechol and kinetic parameters

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Conversion (wt %)</th>
<th>Selectivity (wt %)</th>
<th>TON</th>
<th>(R_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported catalyst</td>
<td>39.1</td>
<td>93.2</td>
<td>8.69</td>
<td>1.28</td>
</tr>
<tr>
<td>Polymer-supported catalyst</td>
<td>60.1</td>
<td>94.1</td>
<td>13.51</td>
<td>1.99</td>
</tr>
</tbody>
</table>

\[\text{H}_2\text{O}_2/\text{[Phenol]}/\text{[Catalyst]}=0.05\text{M}, \text{Time}=1440\ \text{min}, \text{Temp.}=70\ ^\circ\text{C}, \text{CH}_3\text{CN}=2.0\ \text{mL}, \text{TON} \text{in terms of } g\ \text{mol}^{-1}\text{M}hr^{-1}, \text{Rate of oxidation} (\text{R}_p) \text{in terms of } 10^3\ \text{mole dm}^{-3}\ \text{s}^{-1}\]

3.5. Effect of the \(\text{H}_2\text{O}_2\) Concentration / Phenol Concentration /Catalyst Concentration on the Oxidation of Phenol

The oxidation of phenol was 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 70 \(^\circ\text{C}\). When the molar ratio of \(\text{H}_2\text{O}_2\) was varied from 0.5 to 1.0, the oxidation of phenol increased in the presence of supported 3-MHBdMBn Schiff base complex of nickel(II) (Figure 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 showed a decreasing trend, and a similar trend was observed with unsupported 3-MHBdMBn-Ni Schiff base complex analogue. The decreasing trend in the conversion of phenol was due to the decrease in molar ratio of phenol and catalyst with respect to molar ratio of \(\text{H}_2\text{O}_2\).

The catalytic efficiency of the 3-MHBdMBn Schiff base nickel ion complexes in the oxidation of phenol was evaluated at different molar ratios of phenol in the reaction mixture, whereas the molar ratio of \(\text{H}_2\text{O}_2\) to the catalyst was kept constant. The molar ratio of phenol was varied from 0.5 to 2.0 with respect to the molar ratio of \(\text{H}_2\text{O}_2\) to the catalyst. During the molar ratio variation of phenol, the concentration of \(\text{H}_2\text{O}_2\) and the catalyst was kept constant (0.05M). When the molar ratio of phenol was increased from 0.5 to 1.0 in the reaction mixture, the conversion (%) of phenol increased substantially with polymer supported nickel complex of the Schiff base (Figure 6), but when the molar ratio of phenol increased further (>1), the conversion (%) of phenol showed a decreasing trend, which was due to the significant decrease in the molar ratio of \(\text{H}_2\text{O}_2\) to the catalyst in the reaction mixture in comparison with the molar ratio of phenol.

The oxidation of phenol was also evaluated at different molar ratios of polymer-supported 3-MHBdMBn Schiff base complex of nickel at a constant molar ratio (1:1) of the substrate and oxidant. The molar ratio of Schiff base complex of nickel(II) ions was varied from 0.5 to 2.0 at a constant molarity (0.05M) of phenol and \(\text{H}_2\text{O}_2\) in the reaction mixture. The conversion (%) of phenol also showed the same trend as variation of substrate concentration.

3.6. Mechanism for Oxidation of Phenol

Considering the experimental findings for the oxidation of phenol with free and supported 3-MHBdMBn Schiff base complex of nickel ion, the following reaction steps are proposed (Scheme 8). The free and polymer-supported Schiff base complexes of nickel ion (3-MHBdMBn-Ni) have produced active species (Ni-3-MHBdMBn-HOO\(^{\cdot}\)) through fast interactions with hydrogen peroxide and 3-MHBdMBn Schiff base. The active species was subsequently used in the formation of intermediates (Ni-3-MHBdMBn-Ph-HOO\(^{\cdot}\)) through its interactions with phenol in a rapid equilibrium (k). The intermediate (Ni-3-MHBdMBn-Ph-HOO\(^{\cdot}\)) has facilitated the nucleophilic attack of OOH species on ortho and para position on phenol to produce hydroxy-substituted phenols (Scheme 7). The reaction products, catalyst and hydroxyl ions were formed through decomposition of intermediates (Scheme 8 step 4) and finally the hydroxyl ions reacted with hydrogen ions, which were produced in step 1.

![Figure 6. Effect of \(\text{H}_2\text{O}_2\) concentration / phenol concentration /catalyst concentration on oxidation of phenol in presence of polymer-supported nickel complex](image-url)
Ni-3-MHBdMBn-Ph-OOH

The presence of polymer-supported nickel complex. The polymer support has played a significant role in increasing the molar ratio of phenol to hydrogen peroxide and catalyst. Oxidation of phenol was maximum at a molar ratio of 1:1:1. Concentration on oxidation of phenol has great role in concentration / phenol concentration / catalyst. 

Grateful to Ravenshaw University, Cuttack, KIIT University, Bhubaneswar and National Institute of Technology, Raipur for providing research facilities.

Supported 3-MHBdMBn Schiff base complexes of nickel and characterized successfully for their structures and complexes of 3-MHBdMBn Schiff base were synthesized. Effect of H$_2$O$_2$ catalytic activity in the oxidation of phenol. The polymer-supported nickel complexes: Clean and recyclable catalysts. Inorg. Chem. 2005; 43: (6) 252:1420-1450.

The unsupported and polymer-supported nickel complexes of 3-MHBdMBn Schiff base were synthesized and characterized successfully for their structures and catalytic activity in the oxidation of phenol. The polymer-supported 3-MHBdMBn Schiff base complexes of nickel ion showed high catalytic activity than free analogue. The oxidation of phenol showed high selectivity for CTL. The supported catalysts showed high rate of oxidation and TON than unsupported catalysts, which clearly suggested that polymer support has played a significant role in increasing the rate for oxidation of phenol in the presence of metal complexes of 3-MHBdMBn Schiff base. Effect of H$_2$O$_2$ concentration / phenol concentration / catalyst concentration on oxidation of phenol has great role in presence of polymer-supported nickel complex. The oxidation of phenol was maximum at a molar ratio of 1:1:1 molar ratio of phenol to hydrogen peroxide and catalyst.

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References


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Ref.: Ms. No. JCSC-D-14-00111R2
Polymer Supported Nickel Complex: Synthesis, Structure, and Catalytic Application
Journal of Chemical Sciences

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Kumara Swamy K. C.
Associate Editor
Journal of Chemical Sciences

Thank you for submitting your work to this journal.

With kind regards,

N. Periasamy, Ph.D.
Editor-in-Chief
Journal of Chemical Sciences

Journal of Chemical Sciences
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Polymer Supported Nickel Complex: 
Synthesis, Structure, and Catalytic Application

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**Running Title:** Catalytic activity of polymer supported nickel complex

**Keywords:** polystyrene support; catalysis; organometallic catalyst, nickel complex; phenol oxidation

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Abstract

In this work, a new synthetic route for a novel recyclable free [3-MOBDmBn-Ni] and polystyrene anchored [P-3-MOBDmBn-Ni] nickel complexes is presented. These free and polymer anchored metal complexes are synthesized by the reactions of nickel solution with one molar equivalent of unsupported 3-MOBDmBn (N, N’-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine) or polymer supported (P-3-MOBDmBn) Schiff-base ligand in methanol under nitrogen atmosphere. In contrast with other polymer-supported catalysts, the greatest advantage of this catalyst system was that the cost of the catalyst was exceptionally low and recycled up to six times, due to the easily available materials and the simple synthetic route. The higher competence of complexation of nickel on the polymer anchored 3-MOBDmBn Schiff base than unsupported analogue was another advantages of this catalyst system. The structural study reveal that nickel(II) complex of 3-MOBDmBn is square planar in geometry. The catalytic activity of nickel complex towards the oxidation of phenol is investigated in the presence of hydrogen peroxide. Experimental results indicate that the reactivity of P-3-MOBDmBn-Ni is dramatically affected by the polymer support over 3-MOBDmBn-Ni and the rate of oxidation (R_p) for unsupported one is $1.37 \times 10^{-6}$ mole dm$^{-3}$ s$^{-1}$ and for supported analogue is $2.33 \times 10^{-6}$ mole dm$^{-3}$ s$^{-1}$. 
Graphical Abstract

The catalytic activity of free [3-MOBdMBn-Ni] and polystyrene anchored [P-3-MOBdMBn-Ni] nickel complexes are tested towards oxidation of phenol and the effect of the H₂O₂ concentration / phenol concentration /catalyst concentration is presented.

1.0 INTRODUCTION

During the past decades, Schiff base catalysts have had great impact on both the scholastic research works and polymer industry. Schiff base complexes have shown adaptable applications in different organic transformation reaction such as oxidation,[1-2] epoxidation of olefins,[3-4] and polymerization of ethylenes,[5-6]. However, it was observe that the homogeneous Schiff base catalytic systems have two key disadvantages: (1) the lack of control of product, which causes the reactor fouling and (2) the limitation of its use in solution process. Thus, binding these Schiff base metal catalysts onto polymer supports can offer a promising route to prevail over these drawbacks. In general, the heterogeneous Schiff base catalytic system (or supported system) apparently has a lower activity than its corresponding homogeneous analogue. But polymer supported transition metal complexes have shown high catalytic activity [7–8] in comparison with homogeneous and unsupported catalysts. And also polymer supported catalysts are easily recovered without any substantial loss in their catalytic activity [9-10] but homogeneous catalysts are not recovered easily.
On the other hand removal of ecological pollutants such as phenol through oxidation processes is a move towards that is attracting upward attention [11]. The general methods of phenol removal, that include sorption over natural surfaces like activated carbon [12], or sorption over organophilic clay that was modified with organic polymers [13] exist, is not always enough and thus, the phenol need to oxidize or reduce them to less harmful products is necessary. Oxidation of phenols using various chemical reagents such as, hydrogen peroxide, permanganate, molecular oxygen and ozone, are extensively used [14]. The use of hydrogen peroxide has the benefit of producing oxygen and can be used to supplement biological degradation [15]. The oxidation of phenol using unsupported Schiff base complexes of metal ions is reported,[16] but the oxidation of phenol using polymer-supported transition metal complexes was found to be high [17] in the presence of tert-butyl hydroperoxide (t-BHP). The activity of polymer-supported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions in the oxidation of phenol [18-19] also showed variation with temperature, time, etc, which might be due to the change in concentration of substrate or catalyst.

The oxidation of phenol in the presence of metal complexes of salen and hydrogen peroxide as the oxidant is reported, but catalytic activity of metal complexes of N, N'-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MOBdMBn) Schiff base is not reported in the literature; hence, in these investigations an attempt has been made to prepare polymer-supported nickel complex of 3-MHBdMBn Schiff base and to characterize them for their structures and catalytic activity in the oxidation of phenol in the presence of hydrogen peroxide as an oxidant.
2.0 EXPERIMENTAL

2.1 Materials

Divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai, India and used to anchor synthesized 3-MOBdMBn Schiff base complexes of metal ions. The anhydrous chloro salts of nickel(II) ions were purchased from Ranbaxy, Mumbai, India and used without further purifications. The phenol, hydrogen peroxide (30.0 wt%), 2-hydroxy-3-methoxybenzaldehyde (3-MOBd) and 4-Methylbenzene-1,2-diamine (MBn) were procured from E. Merck, India. Other chemicals and solvents were of analytical grade (>99.0 wt%) and used after purifications with standard methods.[20]

2.2 Characterization of 3-MOBdMBn Schiff base and its metal complexes

IR spectra of 3-MOBdMBn Schiff base and its nickel complex were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of 3-MOBdMBn Schiff base and its nickel complex were recorded with Shimadzu 1601 PC UV–Vis Spectrophotometer by using sample mull in a cuvette. Thermogravimetric analysis (TGA) of 3-MOBdMBn Schiff base and its nickel complex was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 5°C min⁻¹. The loading of metal ions on 3-MOBdMBn Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_{max} of nickel ions. The amount of 3-MOBdMBn Schiff base anchored on polymer beads and its composition were estimated using Haraeus Carlo Ebra 1108 Elemental Analyzer. The ^1H-NMR spectra of 3-MOBdMBn Schiff base and nickel complex were recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d₆ as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (µ) of nickel complex was measured
using Vibrating Sample Magnetometer-155. The molecular weight of 3-MOBdMBn Schiff base and its nickel complex was determined using a Vapor Pressure Osmometer (Merk VAPRO 5600, Germany).

2.3 Synthesis of N, N’-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MOBdMBn) and its metal complexes

The 3-MOBdMBn Schiff base was synthesized modifying the procedure reported in the literature.[21] The reaction mixture containing 2-hydroxy-3-methoxybenzaldehyde (20.00 mmol, 3.043 g) and 4-Methylbenzene-1,2-diamine (10.00 mmol, 1.22 g) in methanol was refluxed at 60°C for about 1hr. The reaction mixture on cooling at low temperature produced light orange red colored crystals, which were filtered and recrystallized with methanol. The metal complexes of 3-MOBdMBn Schiff base were prepared taking 100 ml methanolic solution of mixture of Schiff base (20.00 mmol, 7.81 g) and 20.00 mmol of metal ions in a round bottom flask and refluxing at 60°C. After 8 h, the solution was cooled and crystalline metal complexes were separated from the mother liquor. Finally, metal complexes were recrystallized in methanol and dried in a vacuum desiccator.

2.4 Synthesis of polymer-anchored N, N’-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base and its nickel complex

To prepare polymer-anchored nickel complex of 3-MOBdMBn Schiff base, the N, N’-bis (4-amino-2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine (A-3-MOBdMBn) Schiff base was prepared by carrying out nitrosation and reduction reactions on 3-MOBdMBn Schiff base and then reacting resulted A-3-MOBdMBn Schiff base with cross-linked chloromethylated polystyrene beads. The nitrosation of 3-MOBdMBn Schiff base was carried out using 20.00 mmol (7.81 g) of 3-MOBdMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at -5°C. The resultant N, N’-bis (4-nitroso-2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-3-MOBdMBn) was filtered and washed with hot and cold water to remove reaction impurities. The reduction of
NO-3-MOBdMBn was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of metallic iron, which produced A-3-MOBdMBn Schiff base. To immobilize the prepared A-3-MOBdMBn Schiff base on cross-linked chloromethylated polystyrene, the methanol swollen polymer beads (5.0 g) were refluxed in 50 ml methanol containing 20.00 mmol (8.41 g) A-3-MOBdMBn Schiff base. After 8 h, the 3-MOBdMBn Schiff base-anchored polymer beads were separated and dried in a vacuum desiccator. The amount of 3-MOBdMBn Schiff base loaded on polymer beads was estimated with elemental analysis. Subsequently, the metal ions were loaded by keeping 3-MOBdMBn loaded polymer beads (5.0 g) for 10 h in an aqueous solution (50 ml) of metal ions (20.00 mmol). 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 nickel ion on polymer bead was determined by analysing the loading solution with an Atomic Absorption Spectrometer. The loading of nickel ion on free and polymer-supported 3-MOBdMBn Schiff base was calculated as complexation of nickel ion using the amount of 3-MOBdMBn Schiff base taken initially and the amount of nickel ion loaded on polymer beads.

\[
\text{Complexation of metal ions} = \frac{\text{Amount of nickel ion loaded}}{\text{Amount of Schiff base used for loading}} \times 100
\]

2.5 **Catalytic activity of metal complexes in oxidation of phenol**

To evaluate the catalytic activity of free and polymer-supported nickel complex of 3-MOBdMBn Schiff base, the oxidation of phenol was carried out using hydrogen peroxide as the oxidant at fixed ionic strength (0.10 M) and hydrogen ions concentration (pH 7.0) in the 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 0.05 M phenol (4.70 g). The oxidation of phenol was carried out adding 5.67 g (0.05 M) hydrogen peroxide (30.0 wt%) in the reaction mixture and 2.0 ml chlorobenzene
as an internal standard. The water condenser and supply of nitrogen were attached with reaction flask before starting the heating and stirring (1200 rpm) of reaction mixture. Gas chromatography was used to follow these reactions at different time intervals. The retention time of standards was used to identify the reaction products, and product selectivity was measured using peak areas of reaction products in the chromatograms. The reactions were also carried out taking different molar ratios of substrates, hydrogen peroxide, and catalyst. The rate of oxidation for the oxidation of phenol was determined by studying reactions at different temperatures at constant molar ratios of substrate to $\text{H}_2\text{O}_2$ and catalyst. The reactions were also studied without using catalysts to analyze the effect of catalyst in the oxidation of phenol.

**3.0 RESULTS AND DISCUSSION**

Investigations have revealed that polymer-supported metal complexes are sometimes more catalytic and efficient than free and unsupported analogs. [19-20] The activity of catalysts also showed dependence on properties of polymer supports and amount of loaded catalysts. Thermal stability of catalysts is required to be high, if these catalysts have to be applied in high temperature reactions. Therefore, thermal analysis of supported metal complexes was carried out to evaluate their possible applications in high temperature reactions and to provide a proof for complexation of metal ions with polymer-anchored 3-MOBdMBn Schiff base. The TGA of polymer supported 3-MOBdMBn Schiff base showed a weight loss of 39.1 wt% at 500°C, but its nickel(II) ion complex showed a weight loss of 35.1 wt% at same temperature, which was clear indication that nickel(II) ion complex was more stable than Schiff base (Figure 1).

In addition to thermal analysis, the free and polymer-supported nickel complex of 3-
MOBdMBn Schiff base was also characterized by IR and UV techniques to provide a proof for the complexation of metal ions and to decide the structures and geometry of complex on the basis of elemental analysis and magnetic properties.

3.1 Characterization of \( N, N' \)-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine (3-MOBdMBn) Schiff base

The 3-MOBdMBn Schiff base was obtained by refluxing 2-hydroxy-3-methoxybenzaldehyde (3-MOBd) and 4-Methylbenzene-1,2-diamine (MBn) for 1hr at 60°C in methanol, which produced a substantial yield (91.6 wt%) of 3-MOBdMBn Schiff base (Scheme 1). The IR spectrum (Figure 2) of 3-MOBdMBn Schiff base showed absorption bands at 1609 cm\(^{-1}\) (\( >C = N \)), 1263 cm\(^{-1}\) (\( >C – O \)) phenolic (Figure 2). The elemental analysis of 3-MOBdMBn Schiff base showed (wt%): C = 69.82, N = 7.03 and H = 6.31; Caltd (%): C = 70.75, N = 7.17 and H = 5.68, which corresponded to \( C_{23}H_{22}N_{2}O_{4} \) empirical formula of 3-MOBdMBn Schiff base.

The molecular weight of Schiff base was 389.37 g mol\(^{-1}\) (Caltd 390.43 g mol\(^{-1}\)). The electronic spectra of 3-MOBdMBn Schiff base showed absorption bands at 289 nm and 347 nm, which were assigned to \( \pi \rightarrow \pi^{*} \) and \( n \rightarrow \pi^{*} \) transitions. The \(^1\)H-NMR spectrum of 3-MOBdMBn Schiff base showed signals at \( \delta/\text{ppm} = 2.79(3H), 3.71(6H), 5.13(2H), 6.60(2H), 6.98(2H), 7.35(3H), 7.41(2H) \) and 8.61(2H) which corresponded to the structure of 3-MOBdMBn Schiff base as shown in Scheme 1.

Scheme 1. Synthesis of \( N, N' \)-bis (2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine Schiff base (3-MOBdMBn)
3.2 Synthesis and characterization of N, N'-bis (4-amino-2-hydroxy-3-methoxy benzaldehyde) 4-Methylbenzene-1,2-diamine (A-3-MOBdMBn) Schiff base and its anchoring on polymer beads

The nitrosation of 3-MOBdMBn Schiff base was carried out in the presence of NaNO₂/HCl, which gave 87.5% yield of N, N'-bis (4-nitroso-2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-3-MOBdMBn) (Scheme 2). The elemental analysis of N, N'-bis (4-nitroso-2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine showed (wt%): C = 62.01, N = 12.17, and H = 4.95; Calcd (wt%): C = 61.60, N = 12.49, and H = 4.50, which corresponded to C₂₃H₂₀N₄O₆ formula of nitrosated Schiff base. The molecular weight of NO-3-MOBdMBn was 447.02 g mol⁻¹ (Calcd 448.43 g mol⁻¹). The IR spectrum of NO-3-MOBdMBn showed absorption bands at 1604 cm⁻¹ (C=N), 1260 cm⁻¹ (C=O)phenolic, and 1533 cm⁻¹ and 1310 cm⁻¹ for N–O group.

The nitrosation of 3-MOBdMBn Schiff base showed a shift in NMR signals in comparison to NMR signals observed with pure 3-MOBdMBn Schiff base. The nitrosated 3-MOBdMBn Schiff base showed proton signals at δ/ppm = 2.82(3H), 3.75(6H), 5.15(2H), 7.15(2H), 7.36(3H), 7.66(2H) and 8.64(2H), which corresponded to the structure of nitrosated 3-MOBdMBn Schiff base as shown in Scheme 2. The protons ortho to nitroso group in 3-MOBdMBn Schiff base were deshielded; hence, their signals appeared at 7.15 and 7.66 ppm in place of 6.60 and 7.41 ppm respectively, of pure 3-MOBdMBn Schiff base. The proton signal at 6.98 ppm was missing due to the substitution of nitroso group in the benzene.

The NO-3-MOBdMBn was reduced with iron(III) ions in the presence of hydrochloric acid, which gave 81.3 wt% yield of A-3-MOBdMBn Schiff base as shown in Scheme 2. The A-3-MOBdMBn Schiff base was characterized. The elemental analysis of A-3-MOBdMBn Schiff base showed (wt%): C = 63.92, N = 13.21, and H = 7.02, Calcd (wt%): C = 65.70, N = 13.33, and H = 5.75, which corresponded to C₂₃H₂₀N₄O₄ empirical formula of Schiff base. The molecular weight of A-3-MOBdMBn Schiff base was found to be 418.23 g mol⁻¹.
The IR spectrum of A-3-MOBdMBn Schiff base showed absorption bands at 1600 cm\(^{-1}\) (>C= N), 1255 cm\(^{-1}\) (>C–O) phenolic, and a band between 1641 and 1619 cm\(^{-1}\) for >C–N group. The 1H-NMR spectrum of A-3-MHBdMBn Schiff base showed proton signals at \(\delta/\text{ppm} = 2.81(3\text{H}), 3.72(6\text{H}), 4.15(4\text{H}), 5.15(2\text{H}), 6.16(2\text{H}), 6.46(2\text{H}), 7.36(3\text{H})\) and 8.63(2H), which corresponded to the structure of A-3-MOBdMBn Schiff base as shown in Scheme 2.

Scheme 2. Synthesis of \(N, N'\)-bis (4-amino-2-hydroxy-3-methoxybenzaldehyde) 4-Methylbenzene-1,2-diamine (A-3-MOBdMBn) Schiff base

The synthesized A-3-MOBdMBn Schiff base was anchored on cross-linked chloromethylated polystyrene beads by refluxing A-3-MOBdMBn Schiff base with polymer beads in DMF for 8 h at 60°C. The amount of A-3-MOBdMBn Schiff base anchored on polymer beads was 88.1 wt\% (Scheme 3). The anchoring of A-3-MOBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of 3-MOBdMBn Schiff base
anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1594 cm\(^{-1}\) (\(>\text{C}=\text{N}\)), 1246 cm\(^{-1}\) (\(>\text{C}–\text{O}\)) phenolic, and a broadband between 1644 cm\(^{-1}\) (\(>\text{C}=\text{N}\)), which were absent in the IR spectrum of pure polymer beads, but were present in free Schiff base. The IR spectrum of pure polymer beads showed absorption band at 1262 cm\(^{-1}\), which is attributed to \(\text{C}–\text{Cl}\) bond of chloromethyl in cross-linked polymer beads. The decrease in the intensity of absorption band at 1262 cm\(^{-1}\) in polymer-anchored 3-MOBdMBn Schiff base than pure polymer beads was an evidence for anchoring of 3-MOBdMBn Schiff base on polymer beads. The appearance of new absorption bands and shift in characteristic absorption bands of 3-MOBdMBn Schiff base were also used as evidence for anchoring of 3-MOBdMBn Schiff base on polymer beads.

### 3.3 Characterization of free and polymer-anchored metal complexes of 3-MOBdMBn Schiff base

The loading of nickel ion on free and polymer-supported 3-MOBdMBn Schiff base was carried out by refluxing free Schiff base (Scheme 4) and polymer-anchored Schiff base in solution of metal salt at 60\(^{\circ}\)C for 6 h (Scheme 5). The metal complexes of free Schiff base (3-MOBdMBn-Ni) and polymer-anchored Schiff base (P-3-MOBdMBn-Ni) after separation and purification were analyzed for their structures and loading of nickel ion. The complexation of nickel(II) ion on free 3-MOBdMBn Schiff base and polymer-anchored Schiff base was 86.34 and 89.88 wt% respectively (Table 1). These results have clearly suggested that the loading of nickel ion on polymer-supported 3-MOBdMBn Schiff base was higher than free 3-MOBdMBn Schiff base.

![Nickel Salt Solution reflux, rt](image-url)
Scheme 4. Loading of nickel ion on unsupported 3-MOBDMBn Schiff base.

![Scheme 4](image)

Scheme 5. Loading of nickel ion on polymer-supported Schiff base (P-3-MOBDMBn-Ni).

The complexation of nickel ion with 3-MOBDMBn Schiff base showed significant variations in IR 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 complex. The disappearance of phenolic broad band in the IR spectrum of 3-MOBDMBn Schiff base after the complexation of nickel ion was an evidence for the complexation of metal ions with 3-MOBDMBn Schiff base. The polymer-supported Schiff base showed absorption bands at low frequency (Figure 3) in comparison to free Schiff base (Figure 2). On complexation with nickel(II) ion, the frequency of >C=N absorption band of free Schiff base has decreased from 1609 to 1595 cm⁻¹, whereas polymer-supported Schiff base showed variation from 1594 to 1582 cm⁻¹ (Figure 4).

These variations in IR band corresponding to >C=N group of 3-MOBDMBn Schiff base were used as evidence for interactions of metal ions with azomethine nitrogen (>C=N) of 3-MOBDMBn Schiff base. The complexation of nickel(II) ions showed new absorption band at 424 cm⁻¹ with free Schiff base and at 417 cm⁻¹ with polymer-anchored Schiff base, which was due to the formation of M–N bond between nickel(II) ion and Schiff base. The complexation of nickel(II) ion showed another new band due to the formation of bond between nickel and phenolic oxygen (–O–M) with polymer-supported 3-MOBDMBn.
Schiff base at 518 cm\(^{-1}\) (Figure 4).

The complexation of metal ions with Schiff base was further confirmed by comparing electronic spectra of nickel complex and pure 3-MOBdMBn Schiff base. The complexation of nickel(II) ion with 3-MOBdMBn Schiff base showed variation in \(\pi \rightarrow \pi^*\) transition from 289 nm to 280 nm and (Table 2) the \(n \rightarrow \pi^*\) transition of 3-MOBdMBn Schiff base was changed from 347 nm to 299 nm. The charge transfer (CT) and d \(\rightarrow\) d transitions were also used as evidence for complexation of nickel with Schiff base. These electronic transitions corresponded to \(t_{2g}^6\) \(e_g^2\) configurations for nickel(II) ion in this complex.

The magnetic moment (\(\mu\)) of nickel Schiff base complex was found to be 0.83 BM, which indicated that nickel(II) ion complex was diamagnetic in nature with zero unpaired electron.

The magnetic moment (\(\mu\)) and electronic configurations have suggested a square planar structure with dsp\(^2\) hybridization for nickel complex (Scheme 6).

\[\text{Scheme 6. Geometry and structure of 3-MOBdMBn Schiff base complex of nickel ion.}\]

### 3.4 Oxidation of phenol

The catalytic activity of free and polymer-supported nickel complex of 3-MOBdMBn Schiff base was evaluated by studying the oxidation of phenol in the presence of hydrogen peroxide. The gas chromatographic analysis was used to determine the product selectivity and to estimate the percent conversion of phenol. The catechol (CTL) was a major reaction product in the oxidation of phenol (Scheme 7). The formation of reaction products was attributed to enzymatic behaviour of metal complexes of 3-MOBdMBn Schiff base.
Scheme 7. oxidation of phenol.

The polymer support has facilitated the decomposition of these intermediates; hence, per cent conversion of phenol was more with polymer-supported nickel complex (Figure 5) in comparison to free complex of 3-MOBdMBn Schiff base (Table 3). The conversion of phenol was initially high at 240 min and then after the conversion became almost constant due to substantial decrease in the concentration of oxidant and substrate in the reaction mixture (Table 3). Similar trends in substrate conversion were observed with supported catalysts at different time intervals as found with unsupported catalysts (Figure 5 & Table 3). The oxidation reaction also had shown dependence on type of catalyst. The high activity of metal complexes on polymer support was due to the facile interactions of catalyst with substrate than 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 sum of amount of CTL and hydroquinone (HQ) produced, which discarded the formation of other reaction products such as polymeric phenols.

The amount of CTL and HQ was equal to phenol conversion, but reaction showed high selectivity for CTL. The supported catalysts were recycled and also further evaluated for their catalytic activity after their applications in oxidation reactions. The efficiency of supported catalysts remained almost constant upto six recycles and then the efficiency decreased (Table 4). The product selectivity for CTL remained unaffected on using recycled catalysts, which was an indication for the structural stability of metal complexes on polymer support as confirmed by comparing IR spectra of recycled catalysts.
with IR spectra of freshly prepared catalysts. The activity of metal complexes in substrate conversion and product selectivity was evaluated at different molar ratios of substrate to hydrogen peroxide and catalyst.

The rate of phenol conversion was high (2.33 $\times$ 10$^{-6}$ mole dm$^{-3}$ s$^{-1}$) in the presence of polymer-supported 3-MOBdMBn Schiff base complexes of nickel(II) ion than unsupported Schiff base analogue (1.37 $\times$ 10$^{-6}$ mole dm$^{-3}$ s$^{-1}$) (Table 5). The turnover number (TON) for the oxidation of phenol was high (15.82 g mol$^{-1}$Ni hr$^{-1}$) in the presence of polymer supported Schiff base complex in comparison to unsupported Schiff base complex (9.33 g mol$^{-1}$Ni hr$^{-1}$) at a molar ratio of 1:1:1 of H$_2$O$_2$ to phenol and catalyst (Table 5). The rate of substrate conversion and TON in the oxidation of phenol varied significantly with molar ratio of hydrogen peroxide but product selectivity in both cases remained almost constant (Tables 5).

### 3.5 Effect of the H$_2$O$_2$ concentration / phenol concentration /catalyst concentration on the oxidation of phenol

The oxidation of phenol was studied with the variation of the molar ratio of H$_2$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 70°C. When the molar ratio of H$_2$O$_2$ was varied from 0.5 to 1.0, the oxidation of phenol increased in the presence of supported 3-MOBdMBn Schiff base complex of nickel(II) (Figure 6). However, when the molar ratio of H$_2$O$_2$ was further increased (>1) in the reaction mixture, the oxidation of phenol showed a decreasing trend, and a similar trend was observed with unsupported 3-MOBdMBn-Ni Schiff base complex analogue. The decreasing trend in the conversion of phenol was due to the decrease in molar ratio of phenol and catalyst with respect to molar ratio of H$_2$O$_2$.

The catalytic efficiency of the 3-MOBdMBn Schiff base nickel ion complexes in the oxidation of phenol was evaluated at different molar ratios of phenol in the reaction mixture,
whereas the molar ratio of \( H_2O_2 \) to the catalyst was kept constant. The molar ratio of phenol was varied from 0.5 to 2.0 with respect to the molar ratio of \( H_2O_2 \) to the catalyst. During the molar ratio variation of phenol, the concentration of \( H_2O_2 \) and the catalyst was kept constant (0.05M). When the molar ratio of phenol was increased from 0.5 to 1.0 in the reaction mixture, the conversion (%) of phenol increased substantially with polymer supported nickel complex of the Schiff base (Figure 6), but when the molar ratio of phenol increased further (>1), the conversion (%) of phenol showed a decreasing trend, which was due to the significant decrease in the molar ratio of \( H_2O_2 \) to the catalyst in the reaction mixture in comparison with the molar ratio of phenol. The oxidation of phenol was also evaluated at different molar ratios of polymer-supported 3-MOBdMBn Schiff base complex of nickel at a constant molar ratio (1 : 1) of the substrate and oxidant. The molar ratio of Schiff base complex of nickel(II) ions was varied from 0.5 to 2.0 at a constant molarity (0.05M) of phenol and \( H_2O_2 \) in the reaction mixture. The conversion (%) of phenol also showed the same trend as variation of substrate concentration.

### 3.6 Mechanism for oxidation of phenol

Considering the experimental findings for the oxidation of phenol with free and supported 3-MOBdMBn Schiff base complex of nickel ion, the following reaction steps are proposed (Scheme 8). The free and polymer-supported Schiff base complexes of nickel ion (3-MOBdMBn-Ni) have produced active species (Ni-3-MOBdMBn-HOO`) through fast interactions with \( H_2O_2 \) and 3-MOBdMBn Schiff base. The intermediate (Ni-3-MOBdMBn-Ph-HOO`) has facilitated the nucleophilic attack of `OOH` species on ortho and para position on phenol to produce hydroxy-substituted phenols (Scheme 7). The reaction products, catalyst and hydroxyl ions were formed through decomposition of intermediates (Scheme 8 step 4) and finally the hydroxyl ions reacted with hydrogen ions, which were produced in step 1.
4.0 CONCLUSION

The unsupported and polymer-supported nickel complexes of 3-MOBdMBn Schiff base were synthesized and characterized successfully for their structures and catalytic activity in the oxidation of phenol. The polymer-supported 3-MOBdMBn Schiff base complexes of nickel ion showed high catalytic activity than free analogue. The oxidation of phenol showed high selectivity for CTL. The supported catalysts showed high rate of oxidation and TON than unsupported catalysts, which clearly suggested that polymer support has played a significant role in increasing the rate for oxidation of phenol in the presence of metal complexes of 3-MOBdMBn Schiff base. Effect of H₂O₂ concentration / phenol concentration / catalyst concentration on oxidation of phenol has great role in presence of polymer-supported nickel complex. The oxidation of phenol was maximum at a molar ratio of 1:1:1 molar ratio of phenol to hydrogen peroxide and catalyst.

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REFERENCES

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**Figure Captions**

**Figure 1** Thermal stability of polymer-supported 3-MOBdMBn Schiff base and its nickel complex.

**Figure 2** FTIR spectra of unsupported 3-MOBdMBn Schiff base

**Figure 3** FTIR spectra of polymer supported 3-MOBdDBn Schiff base

**Figure 4** FTIR spectra of polymer supported 3-MOBdDBn-Ni complex.

**Figure 5** Effect of reaction time on oxidation of phenol in presence of polymer-supported and unsupported nickel complexes. [Phenol]:[Catalyst]: [H₂O₂] = 1:1:1 (0.05M), Temp. = 70 °C

**Figure 6** Effect of H₂O₂ concentration / phenol concentration /catalyst concentration on oxidation of phenol in presence of polymer-supported nickel complex.

**Table Captions**

**Table 1** Efficiency of complexation (EC) of nickel ion (wt%)

**Table 2** Electronic transitions in unsupported and polymer supported nickel complex of 3-MOBdMBn Schiff base

**Table 3** Catalytic activity of unsupported and polymer supported nickel complex (Ni-3-MOBdMBn) in oxidation of phenol (Ph).

**Table 4** Efficiency of recycled supported catalysts (P-3-MOBdMBn-M) in oxidation of phenol.

**Table 5** Oxidation of phenol by nickel complex of 3-MOBdMBn Schiff base: Phenol conversion, selectivity for catechol and kinetic parameters
Figure 1. Thermal stability of polymer-supported 3-MOBdMBn Schiff base and its nickel complex.

Figure 2. FTIR spectra of unsupported 3-MOBdDMBn Schiff base
Figure 3. FTIR spectra of polymer supported 3-MOBdDBn Schiff base.

Figure 4. FTIR spectra of polymer supported 3-MOBdDBn-Ni complex.
Figure 5. Effect of reaction time on oxidation of phenol in presence of polymer-supported and unsupported nickel complexes. [Phenol]:[Catalyst]:[H₂O₂] = 1:1:1 (0.05M), Temp. = 70°C.

Figure 6. Effect of H₂O₂ concentration / phenol concentration /catalyst concentration on oxidation of phenol in presence of polymer-supported nickel complex.
Table 1. Efficiency of complexation (EC) of nickel ion (wt%)

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>Complexation (EC) of nickel(II) ion (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported 3-MOBDMBn Schiff base</td>
<td>86.34</td>
</tr>
<tr>
<td>Polymer supported 3-MOBDMBn Schiff base</td>
<td>89.88</td>
</tr>
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</table>


Table 2. Electronic transitions in unsupported and polymer supported nickel complex of 3-MOBDMBn Schiff base

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Frequencies $\lambda_{\text{max}}$ / nm</th>
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<tr>
<td></td>
<td>$\pi\rightarrow\pi^*$</td>
</tr>
<tr>
<td>3-MOBDMBn</td>
<td>289</td>
</tr>
<tr>
<td>P-3-MOBDMBn</td>
<td>282</td>
</tr>
<tr>
<td>3-MOBDMBn -Ni</td>
<td>280</td>
</tr>
<tr>
<td>P-3-MOBDMBn -Ni</td>
<td>273</td>
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Table 3. Catalytic activity of unsupported and polymer supported nickel complex (Ni-3-MOBdMBn) in oxidation of phenol (Ph).

<table>
<thead>
<tr>
<th>Time/min</th>
<th>P-3-MOBdMBn-Ni</th>
<th>3-MOBdMBn-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>13</td>
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</tr>
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<td>30</td>
<td>33.8</td>
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<tr>
<td>60</td>
<td>45.9</td>
<td>26.6</td>
</tr>
<tr>
<td>90</td>
<td>57.6</td>
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<td>40.5</td>
</tr>
<tr>
<td>1440</td>
<td>68.8</td>
<td>41.1</td>
</tr>
</tbody>
</table>

[Phenol]:[Catalyst]: [H\textsubscript{2}O\textsubscript{2}] = 1:1:1 (0.05M), Temp. = 70 °C. CH\textsubscript{3}CN = 2.0 mL.

Table 4. Efficiency of recycled supported catalysts (P-3-MOBdMBn-M) in oxidation of phenol.

<table>
<thead>
<tr>
<th>Supported metal complexes</th>
<th>Recycle number</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>P-3-MHBdMBn -Ni</td>
<td>Conversion</td>
</tr>
<tr>
<td></td>
<td>Selectivity</td>
</tr>
</tbody>
</table>

[Phenol]:[Catalyst]: [H\textsubscript{2}O\textsubscript{2}] = 1:1:1 (0.05M), Temp. = 70 °C. CH\textsubscript{3}CN = 2.0 mL.
Table 5. Oxidation of phenol by nickel complex of 3-MOBdMBn Schiff base: Phenol conversion, selectivity for catechol and kinetic parameters

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Conversion (wt%)</th>
<th>Selectivity (wt%)</th>
<th>TON</th>
<th>R&lt;sub&gt;p&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported catalyst</td>
<td>41.1</td>
<td>94.2</td>
<td>9.33</td>
<td>1.37</td>
</tr>
<tr>
<td>Polymer-supported catalyst</td>
<td>68.8</td>
<td>95.1</td>
<td>15.82</td>
<td>2.33</td>
</tr>
</tbody>
</table>

[H<sub>2</sub>O<sub>2</sub>] /[Phenol]/[Catalyst] = 0.05M, Time = 1440 min, Temp. = 70 °C CH<sub>3</sub>CN = 2.0 mL TON in terms of = g mol<sup>-1</sup>M hr<sup>-1</sup>, Rate of oxidation (R<sub>p</sub>) in terms of = 10<sup>-6</sup> mole dm<sup>3</sup>s<sup>-1</sup>