

### 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 ethylenes 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

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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 H<sub>2</sub>O<sub>2</sub>, permanganate, molecular oxygen, and ozone is widely used [16]. The use of H<sub>2</sub>O<sub>2</sub> has the advantage of producing oxygen, which can be used to augment biological degradation [17]. The use of H<sub>2</sub>O<sub>2</sub> 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. H<sub>2</sub>O<sub>2</sub> works either alone or with a catalyst, but the catalytic process gives better results. Fe is the most common homogeneous catalyst used with H<sub>2</sub>O<sub>2</sub> [18]. In the present investigation, phenol oxidation was chosen as the model reaction to study the catalytic activity of the synthesized 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'-bis(2-hydroxy-3-methoxybenzaldehyde)4-methylbenzene-1,2-diamine (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 H<sub>2</sub>O<sub>2</sub> 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, H<sub>2</sub>O<sub>2</sub> (30.0 wt%), 2-hydroxy-3-methoxybenzaldehyde (3-MOBd), and 4-methylbenzene-1,2diamine (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 N,N'bis(4-amino-2-hydroxy-3-methoxybenzaldehyde)-4-methylben zene-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  $\lambda_{max}$ . The compositions of 3-MOBdMBn and its zinc complex were estimated using a Haraeus Carlo Ebra 1108 elemental analyzer. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded with a Bruker FT-NMR 300 MHz spectrometer using DMSO-d<sub>6</sub> 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  $H_2O_2$  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);



Fig. 1. Thermal stability of P-3-MOBdMBn and its zinc complex.

 $H_2O_2$  (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 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 hightemperature 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 zinc(II) ion complex showed a mass loss of 27.0% at the same temperature, clearly indicating that the zinc 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.



Fig. 2. FTIR spectra of unsupported 3-MOBdMBn (1) and polymer-supported P-3-MOBdMBn (2).

#### 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<sup>-1</sup>, which was assigned to phenolic OH. Elemental analysis of 3-MOBdMBn (wt%): C 70.75, N 7.17, and H 5.68; calcd (%): C 69.82, N 7.03, and H 6.31, corresponding to C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>, the empirical formula of 3-MOBdMBn [7,12].

The molecular mass of the Schiff base was 390.43 g/mol (calcd 389.37 g/mol). The electronic spectrum of 3-MOBdMBn (Fig. 3) showed absorption bands at 289 and 347 nm, which were assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The <sup>1</sup>H-NMR spectrum of the Schiff base showed signals at  $\delta$  = 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 nitrosation of 3-MOBdMBn was carried out in the presence of NaNO<sub>2</sub>/HCl, producing NO-3-MOBdMBn in 84.5% yield (Scheme 2); elemental analysis (%): C 61.60, N 12.49, and H 4.50; calcd (%): C 62.01, N 12.17, and H 4.95, corresponding to  $C_{23}H_{20}N_4O_6$ , the formula of the nitrosated Schiff base. The molecular mass of NO-3-MOBdMBn was 448.43 g/mol (calcd 447.02 g/mol). The IR spectrum of NO-3-MOBdMBn showed



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



Fig. 3. Electronic spectra of unsupported 3-MOBdMBn and polymer-supported P-3-MHBdDBn.

absorption bands at 1604 (C=N), 1260 (C-O, phenolic), and 1500 and 1315 cm<sup>-1</sup> 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(III) 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; calcd (%): C 63,92, N 13.21, and H 7.02, corresponding to C<sub>23</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>, the empirical formula of the Schiff base. The molecular mass of A-3-MOBdMBn was 420.46 g/mol (calcd 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<sup>-1</sup> for the C-N group. The <sup>1</sup>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<sup>-1</sup> (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<sup>-1</sup>, 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<sup>-1</sup> 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.



Scheme 3. Synthesis of polymer-anchored Schiff base P-3-MOBdMBn.



Scheme 4. Complexation of zinc ions with free 3-MOBdMBn.



P-3-MOBdMBn-Zn

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

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<sup>-1</sup> 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<sup>-1</sup>, and that of the polymer-supported Schiff shifted from 1594 to 1575 cm<sup>-1</sup> (Fig. 4) [7].

Complexation with zinc(II) ions resulted in a new absorption band at 403 cm<sup>-1</sup> for the free Schiff base and at 401 cm<sup>-1</sup> 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



#### Fig. 4. FTIR spectrum of P-3-MOBdDBn-Zn complex.

#### Table 1

FTIR frequencies and electronic transitions of 3-MOBdMBn and its unsupported and polymer-supported zinc ion complexes.

Compound	Absorption frequency (cm <sup>-1</sup> )					Frequency $\lambda_{max}$ (nm)	
	VC=N	νc-0	νон	νм-0	VM-N	$\pi \rightarrow \pi *$	$n \rightarrow \pi^*$
3-MOBdMBn	1609	1263	2910-3200	_	_	289	347
P-3-MOBdMBn	1594	1246	2900-3340	_	_	282	344
3-MOBdMBn-Zn	1591	1286	_	560	403	265	307
P-3-MOBdMBn-Zn	1575	1278	_	557	401	260	301

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 hypsochromic shift of the  $\pi \rightarrow \pi^*$  transition from 289 to 265 nm, and of the  $n \rightarrow \pi^*$ 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<sup>3</sup> 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<sub>2</sub>O<sub>2</sub>. 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-





**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.

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 H<sub>2</sub>O<sub>2</sub> 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  $(1.64 \,\mu mol/(L \cdot s))$  in

Table 2

Recycle number	Conversion (%)	Selectivity (%)		
0	48.7	90.0		
2	47.3	90.3		
4	45.2	88.6		
6	41.2	84.2		
8	24.4	81.7		

[Phenol] = [Catalyst] = [H<sub>2</sub>O<sub>2</sub>] = 0.05 mol/L, 70 °C, CH<sub>3</sub>CN = 2.0 mL.

#### Table 3

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

Catalant	Conversion	Selectivity	TON	Rate			
Catalyst	(%)	(%)	(g/(mol·h))	(µmol/(L·s))			
3-MOBdMBn-Zn	25.9	89.4	5.83	0.86			
P-3-MOBdMBn-Zn	48.7	90.0	11.14	1.64			
[Phenol] = [Catalyst] = [H <sub>2</sub> O <sub>2</sub> ] = 0.05 mol/L, 1440 min, 70 °C, CH <sub>3</sub> CN =							
2.0 mL							

the presence of the P-3-MOBdMBn-Zn and low (0.86  $\mu$ mol/(L·s)) in the presence of the unsupported analog (Table 3); a similar trend was observed for the turnover number (TON) at H<sub>2</sub>O<sub>2</sub>:phenol:catalyst molar ratio = 1:1:1.

### 3.6. Effect of $H_2O_2$ , phenol, and catalyst concentrations on phenol oxidation

The oxidation of phenol was studied using different molar ratios of  $H_2O_2$  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  $H_2O_2$  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  $H_2O_2$  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  $H_2O_2$ .

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  $H_2O_2$  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  $H_2O_2$  to the catalyst. The concentrations of  $H_2O_2$  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  $H_2O_2$  to the catalyst in the reac-



Fig. 6. Effect of  $H_2O_2$ , phenol, and catalyst concentrations on phenol oxidation in the presence of P-3-MOBdMBn-Zn at 70 °C.



Scheme 7. Reaction steps in phenol oxidation.

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  $H_2O_2$  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<sup>-</sup>, through fast interactions with H<sub>2</sub>O<sub>2</sub> 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  $H_2O_2$ , phenol, and catalyst concentrations on phenol oxidation was important for the polymer-supported zinc complex. Phenol oxidation conversion was maximum at the phenol: $H_2O_2$ :catalyst ratio of 1:1:1.

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The synthesis of a simple, inexpensive, reusable, and highly efficient polymer-supported -ONNO- tetradentate Schiff base zinc(II) ion catalyst for the oxidation of phenol with  $H_2O_2$  to catechol and hydroquinone was described.

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