



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

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ABSTRACT

The free and polymer anchored copper ion complexes [HMBdMBn-Cu and P- HMBdMBn-Cu], supported by -ONNO-tetradentate Schiff-base ligand are prepared by the reactions of metal solution with one molar equivalent of unsupported HMBdMBn (N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine) or polymer supported Schiff-base ligands in methanol. The efficiency of complexation of copper ion on the polymer anchored HMBdMBn Schiff base was more than unsupported one. The structural study reveal that copper(II) ion complex of HMBdMBn Schiff base is square planar geometry. Complexation of copper ion increased the thermal stability of HMBdMBn Schiff base. The catalytic activities of copper complexes toward the oxidation of phenol are investigated in the presence of hydrogen peroxide. Experimental results indicate that the reactivity of P-HMBdMBn-Cu is dramatically affected by the polymer support over HMBdMBn-Cu. The rate of phenol conversion was high ($1.57 \times 10^{-6} \text{ mole dm}^{-3} \text{ s}^{-1}$) in the presence of polymer-supported HMBdMBn Schiff base complexes of copper and low in the presence of unsupported analogue. The TON for polymer supported copper catalyst was found to be $10.64 \text{ g mol}^{-1} \text{ Cu hr}^{-1}$.

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 transnational 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_2O_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. 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 [21]. Heterogeneous catalysts involve metal oxides [22] and supported

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_2O_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_2O_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, Mumbai. The phenol, hydrogen peroxide (30.0 wt%), 2-hydroxy-3-methylbenzaldehyde and 4-Methylbenzene-1,2-diamine were procured from 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 $10^\circ\text{C min}^{-1}$. 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 1hr. 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 were prepared taking 100 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 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 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 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 =

$$\frac{\text{Amount of copper ion loaded}}{\text{Amount of Schiff base used for loading}} \times 100$$

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 5.67 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_2O_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.

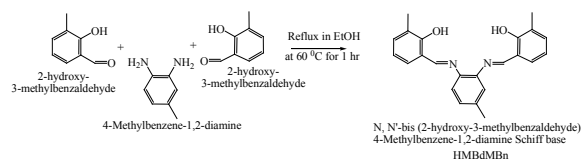
RESULTS AND DISCUSSION

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 = 6.19, which corresponded to $C_{23}H_{22}N_2O_2$ empirical formula of HMBdMBn Schiff base.

The molecular weight of Schiff base was 357.37 $g\ mol^{-1}$ (Caltd 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 $\delta/ppm = 2.52(6H)$, 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.



Scheme 1. Synthesis of HMBdMBn Schiff base

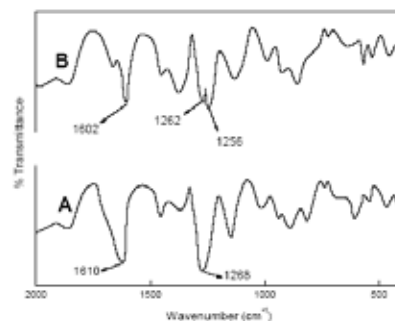
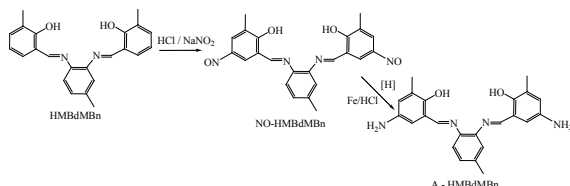


Figure 1. FTIR spectra of unsupported HMBdMBn Schiff base (A) & polymer supported HMBdMBn Schiff base (B).

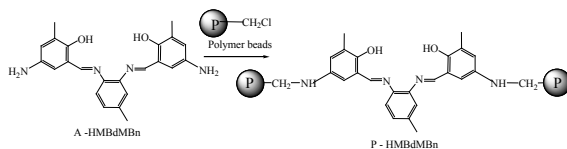
3.2 Synthesis and characterization of A- HMBdMBn Schiff base and its anchoring on polymer beads

The elemental analysis of N, N'-bis (4-nitroso-2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1, 2-diamine 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 $C_{23}H_{20}N_4O_4$ formula of nitrosated Schiff base. 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=N), 1266 cm⁻¹ (>C-O)phenolic, and 1530 cm⁻¹ and 1320 cm⁻¹ for N-O group. The nitrosation 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 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 HMBdMBn Schiff base. The protons ortho to nitroso group in HMBdMBn Schiff base were deshielded; hence, their signals appeared at 7.35 and 7.96 ppm in place of 7.27 and 7.60 ppm respectively, of pure HMBdMBn Schiff base. The proton signal at 6.91 ppm was missing due to the substitution of nitroso 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 $C_{23}H_{24}N_4O_2$ empirical formula of Schiff base. 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 1H-NMR spectrum of A- HMBdMBn 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- HMBdMBn Schiff base as shown in Scheme 2.



Scheme 2. Synthesis of N, N'-bis (4-amino-2-hydroxy-3-methyl benzaldehyde) 4-Methylbenzene-1,2-diamine (A-HMBdMBn) Schiff base

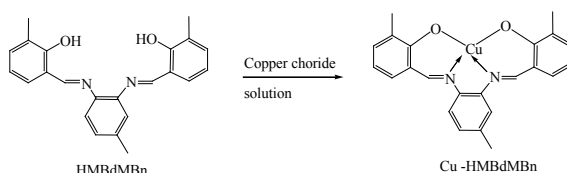
The anchoring of A-HMBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of HMBdMBn Schiff base anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1602 cm⁻¹ (>C=N), 1260 cm⁻¹ (>C-O) phenolic, and a 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 HMBdMBn Schiff base than pure polymer beads was an evidence for anchoring 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 were also used as evidence for anchoring of HMBdMBn Schiff base on polymer beads.



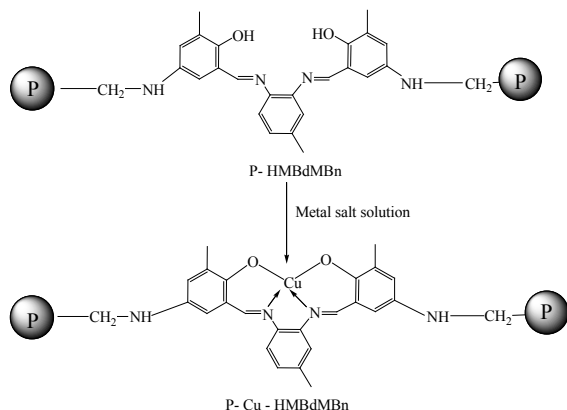
Scheme 3. Synthesis of polymer-anchored Schiff base (P-3-MHBdMBn)

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

The complexation of copper 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).



Scheme 4. Loading of copper ion on unsupported HMBdMBn Schiff base



Scheme 5. Loading of copper ion on polymer-supported Schiff base (P- HMBdMBn-Cu)

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 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 $\pi \rightarrow \pi^*$ transition from 284 nm to 277 nm, and for the $n \rightarrow \pi^*$ 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 $d \rightarrow d$ transitions. These electronic transitions corresponded to $t_{2g}^6 e_g^3$ configurations for copper(II) ion in this complex. The magnetic moment (μ) of Schiff base complexes of copper(II) ion was found to be 1.81BM, which indicated that copper(II) ion complex was paramagnetic in nature with one unpaired electron. The magnetic moment (μ) and electronic configu-

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

Compounds	Frequencies λ_{max} / nm			
	$p \rightarrow p^*$	$n \rightarrow \pi^*$	C \rightarrow T	d \rightarrow d
HMBdMBn	284	346	-	-
P- HMBdMBn	281	341	-	-
HMBdMBn -Cu	277	307	354	561
P- HMBdMBn -Cu	271	301	349	557

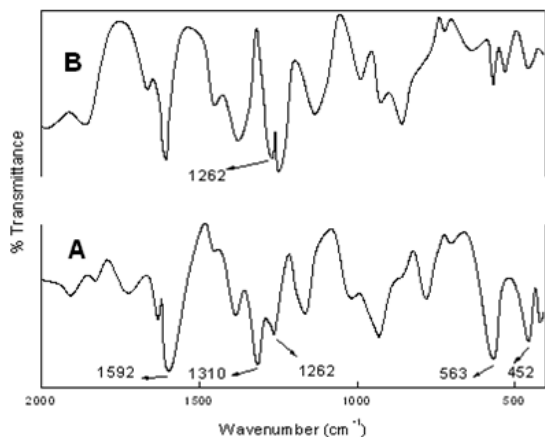
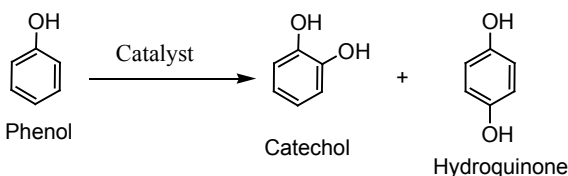


Figure 2. FTIR spectra of polymer supported HMBdMBn-Cu complex (A) and polymer supported HMBdMBn Schiff base ligand (B)

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).



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 upto six recycles and then the efficiency decreased (Table 3). The product selectivity for catechol remained unaffected on 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.

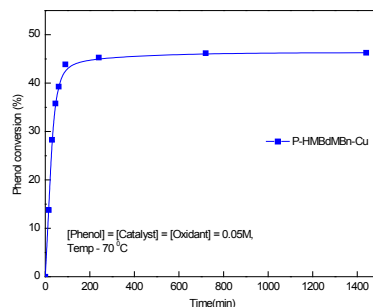


Figure 3. Effect of reaction time on oxidation of phenol in presence of polymer-supported copper complexes.

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

Time/min	Cu-HMBdMBn
0	0.0
15	4.7
30	10.0
45	18.1
60	23.9
90	28.3
240	30.0
720	30.6
1440	31.3

[Phenol]:[Catalyst]: [H₂O₂] = 1:1:1 (0.05M), Temp. = 70 °C. CH₃CN = 2.0 mL.

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

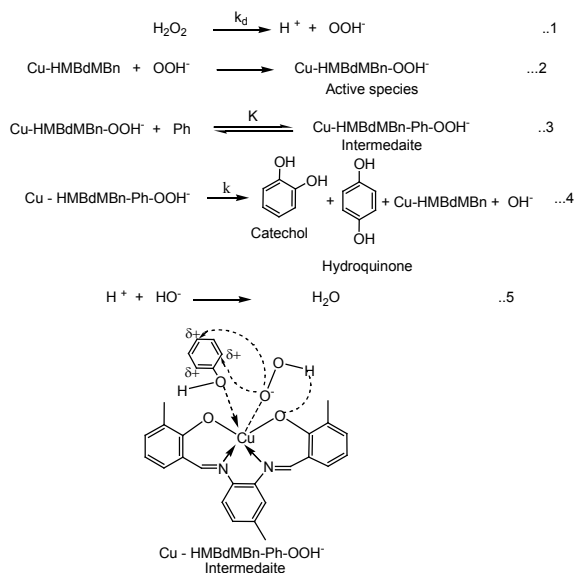
Supported metal complexes	Recycle number					
		0	2	4	6	8
P- HMBdMBn -Cu	Conversion	46.3	46.1	45.9	42.4	33.2
	Selectivity	91.3	91.0	90.4	88.7	85.8

[Phenol]:[Catalyst]: [H₂O₂] = 1:1:1 (0.05M), Temp. = 70 °C. CH₃CN = 2.0 mL.

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

CONCLUSIONS

Polymer-supported copper-ion complex of the HMBdMBn Schiff base was synthesized and characterized for their structures and catalytic activity in the oxidation of phenol. The polymer-supported HMBdMBn Schiff base complex of copper showed higher catalytic activity than the unsupported copper complex. Phenol was selectively oxidized to catechol with unsupported and polymer supported HMBdMBn Schiff base complex of copper in the presence of H_2O_2 as an oxidant. The supported catalyst showed a significant increase turn over number and rate of oxidation for the oxidation of phenol in comparison with the unsupported catalysts, and this clearly suggested that the polymer support was able to improve the catalytic activity of Schiff base complexes of copper ions. The supported catalyst was reusable up to six recyclings without any loss in their activity.

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