

Green and efficient hydroxylation of phenol using H₂O₂ catalyzed by coordination polymers

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ABSTRACT

New two coordination polymers, *viz.* [-CH₂(Cu(bis-salan))-]_n and [-CH₂(Mn(bis-salan).2H₂O)-]_n, where salan = 5,5'-methylene bis-salicylideneaniline were synthesized and characterized. These coordination polymers were evaluated as heterogeneous catalysts for the liquid-phase hydroxylation of phenol using a green oxidant H₂O₂. The optimized reaction conditions were studied through variation of process parameters such as temperature, time, type of oxidants and solvents, volume of solvent, amount of catalyst and phenol to H₂O₂ molar ratio. The catalytic activity of the synthesized Cu-based catalyst (37 %) is higher than the Mn-based catalysts (22 %), while Mn-based catalyst shows a much higher selectivity to catechol (~96 %) than the Cu-based catalyst (~71 %).

Keywords: green oxidant, hydroxylation of phenol, coordination polymer

1 INTRODUCTION

The hydroxylation of phenol is a field of great challenge and one of the industrially important reactions and usually gives catechol and hydroquinone; their production is always of great interest to chemists and engineering, in particular for direct phenol hydroxylation by hydrogen peroxide, which is environmentally benign process.

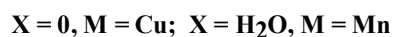
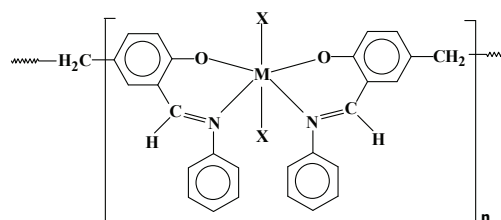
Over the years, several oxidants have been tested for oxidation reactions. Recently more interest toward hydrogen peroxide is rising above other oxidants due to environmental precautions. The choice of H₂O₂ as an oxidant is motivated by its ease and safe handling, moderate cost and high active oxygen content, as well as the fact that water is the only by-product, stimulating its use in liquid-phase oxidations, especially for fine-chemicals production.

Transition metal complexes have been used extensively as homogenous catalysts, however, the main drawback of their applications are the difficult to recover and short life-time. The best method for merging the advantages of homogeneous catalysts (high activity and selectivity) with the advantages of heterogeneous catalysts (easy separation, long catalytic life and selectivity which leads to more

environmentally benign chemical processes) is heterogenization of soluble catalysts to eliminate these disadvantages. Coordination polymers promise industrial applications such as adsorbents, sensors and catalysts [1]. However the applications of coordination polymers as catalysts for hydroxylation of phenol have not been reported widely in the literature.

Recently, numerous heterogeneous catalysts have been attracting research interest and have been used for the hydroxylation of phenol such as microporous and mesoporous materials, TS-1 [2], Cu-MCM-41 [3], TAPO-5, TAPO-11 [4], ternary hydrotalcites and hydrotalcite-like compounds [5,6], heteropoly compounds [7], supported metal complexes [8], and encapsulated metal complexes [9,10]. A few reports are available on hydroxylation of phenol using coordinated polymers as catalysts [11].

As a continuation of research on catalyzed hydroxylation of phenol, we report herein the synthesis and characterization of new two coordination polymers, *viz.* [-CH₂{Cu(bis-salan)}-]_n and [-CH₂{Mn(bis-salan).2H₂O}-]_n, where salan = 5,5'-methylene bis-salicylideneaniline (Structure 1). These coordination polymers were evaluated as heterogeneous catalysts for the liquid-phase hydroxylation of phenol using H₂O₂ as an oxidant. The optimized reaction conditions were studied through variation of process parameters such as temperature, time, type of oxidants and solvents, volume of solvent, amount of catalyst and phenol to H₂O₂ molar ratio.



Structure 1

2 EXPERIMENTAL

2.1 Materials

All chemicals and solvents were of AR grade and used without purification. 5,5'-Methylene bis(salicylaldehyde) was prepared following the procedure [12].

2.2 Physical methods and analyses

The elemental analyses were performed at Elemental Analyser CHN Thermo. The metal content were measured by using GBC Avanta atomic absorption spectrophotometer. The ATR-IR measurements were carried out on a Perkin-Elmer Spectrum 100 FTIR spectrometer. Electronic spectra were recorded on a GBC UV/VIS 920 UV-Visible spectrophotometer in absolute ethanol or in Nujol (by layering the mull of the sample to the inside of one of the cuvette while keeping another one layered with Nujol as reference). The magnetic susceptibility measurement was carried by Gouy method. Scanning Electron Micrographs (SEM) of the catalysts were recorded on Hitachi X-650 EM. Reaction products were analyzed using a Varian CP3800 gas chromatograph fitted with flame ionization detector. A HP-PONA capillary column (50m x 0.35mm x 0.5 μ m film thickness, Agilent technologies). The retention time of all peaks was compared with authentic samples and also the identity of the products was further confirmed by a GC-MS using Finnigan MAT GCQ GC/Mass spectrometer. Thermal studies were carried out on Perkin Elmer Pyris Diamond TG/DTA.

2.3 Synthesis of catalysts

2.3.1 Synthesis of methylene bis-5,5'-(salicylideneaniline) Schiff base ligand

A methanolic solution (10 ml) of aniline (1.86 g, 0.02 mol) was added drop wise in 30 ml methanolic solution of 5,5'-methylene bis(salicylaldehyde) (2.56 g, 0.01 mol) under vigorous stirring. The reaction mixture was refluxed for 2 h, which produced yellow to orange precipitate. After cooling, the precipitate was filtered, washed repeatedly with methanol and then after recrystallization from acetone: methanol mixture (1:1), a brownish yellow solid was obtained.

2.3.2 Synthesis of metal coordinated complexes

The coordinated metal complexes were prepared by refluxing 15 ml of metal acetate in acetone, [M = Co(II) and Mn(II)] (0.003 mol) and 20 ml acetonic solution of methylene bis-5,5'-(salicylideneaniline) (0.003 mol) for 2 h. The crude solid obtained was filtered, washed with hot methanol and acetone then dried at 120 °C.

2.4 Catalytic activity test

In a typical reaction, a mixture of phenol (0.05 mol) and 30 % H₂O₂ (0.05 mol) in 2 ml acetonitrile were kept in a two-necked round bottomed flask maintained at 80 °C, the exact amount (10 mg) of catalyst was added. The resulting mixture was stirred for prescribed time. Liquid samples were periodically drawn from reaction mixture and analyzed by gas chromatograph.

3 RESULTS AND DISCUSSION

Condensation of 5,5'-methylenebis(salicylaldehyde) with aniline in 1:2 molar ratio leads to the formation of Schiff base ligand, methylene bis-5,5'-(salicylidene aniline). The synthesized ligand was subsequently reacted with Cu(II) and Mn(II) acetates to obtain the metal complexes in polymeric form (Scheme 1). The metal ions have acted as bridge between two Schiff base ligands to produce a linear coordination polymeric complex.

3.1 Characterization of catalysts

Both complexes were characterized by a combination of spectroscopic, thermal analyses and micro analysis. The elemental analyses support the formation of complexes as proposed, metal analysis supports the presence of metal ions in each pocket of coordinating atoms.

3.2 Spectral analyses

3.2.1 IR analysis

IR spectrum of the ligand displays a broad band with medium intensity in the frequency range of 2400-2700 cm⁻¹ due to intramolecular hydrogen bonding between phenolic hydrogen and azomethine nitrogen. The absence of this band in the spectra of the coordinated complexes has given indication for deprotonation and subsequent coordination of phenolic oxygen with metal ions. The shift in stretching frequency for C-O band after coordination with metal ions has further supported evidence for the coordination of metal ions with phenolic oxygen of the ligand [13].

The Schiff base ligand has shown a band at 1622 cm⁻¹, which has been assigned to -C=N- azomethine (imino) group of the ligand. Normally the band appears at around 1637 cm⁻¹ but appearance of this band at 1622 cm⁻¹ in the synthesized ligand has been assumed due to the possible intramolecular hydrogen bonding with azomethine nitrogen. On complexation with metal ions, the band corresponding to -C=N bond has shown significant shift to the lower frequency which further supported the coordination of metal ions with azomethine nitrogen.

The coordination of phenolic oxygen and azomethine nitrogen with metal ions is further evident by formation of the observed new bands in the region 550-490 and 475-400

cm^{-1} , which are attributed to M-O and M-N stretching vibrations, respectively [14]. These data have proved the coordination of dianionic Schiff base to metal ions through phenolic oxygen and imine nitrogen. This has also confirmed the tetradentate coordination of Schiff base.

A multiple band centred at 2920 cm^{-1} in the ligand spectrum is attributed to $-\text{CH}_2$ (methylene bridge) group. These bands remained unaffected after coordination with metal ions, which indicated that methylene group remained undisturbed after metal ion coordination.

3.2.2 Electronic spectral analysis

The electronic spectrum of Schiff base ligand $[-\text{CH}_2(\text{H}_2\text{bis-salan})]$ exhibited bands at 206, 237, 279, 308, 321 and 358 nm assigned to $\Phi \rightarrow \Phi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. As molar absorptivity of bands at 308 and 358 nm is comparatively low, these bands have been presumed to be split band of $n \rightarrow \pi^*$ transition. The bands at 308 and 237 nm in the electronic spectra of ligand has been considered due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the phenolic group. The electronic spectra of metal complexes shown almost all bands at nearly same position with slight shift in bands corresponding to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\Phi \rightarrow \Phi^*$ transitions, in comparison to uncomplexed ligand.

The electronic spectrum of $[-\text{CH}_2\{\text{Cu}(\text{bis-salan})\}_n]$ has displayed two new bands at 368 and 439 nm, in which the former band is assignable to symmetry forbidden ligand to metal charge transfer transition (LMCT). The latter band has been considered due to d-d transitions in copper(II) ions of the complex. These data are in agreement with copper complexes of salpn (salpn = salicylaldehyde 1,3-propylenediamine) and salen (salen = salicylaldehyde ethylenediamine) Schiff bases. Therefore, square planar geometry has been assumed for the synthesized copper complex of methylene bis-5,5'-(salicylidene aniline) as observed with salpn and salen [15]. The bands at 240 and 277 nm have been assigned to intra-ligand transitions.

The electronic spectrum of the Mn(II) complex in comparison with electronic spectrum of its ligand has given a new band at 428 nm which has been assigned to ligand-metal charge transfer transitions. Other bands within 232 - 351 nm have been assigned to intra-ligand transitions.

The band expected at 321 nm in Mn(II) complex due to ${}^6\text{A}_{1g} - {}^4\text{E}_g$ (D) transition is masked under the intense ligand centred band, which is characteristic transition for octahedral geometry [16], hence octahedral geometry has been approved for Mn complex.

3.3 Thermal analysis

The thermogravimetric analysis of the complexes has been carried out to investigate their stability. The first weight loss of 2.4 % (calculated 2.6 %) within the temperature range $160\text{--}245\text{ }^\circ\text{C}$ corresponding to the loss of one carbon atom per repeating unit of polymeric copper complex. In the temperature range of $245\text{--}475\text{ }^\circ\text{C}$, the

complex has shown significant weight loss in two steps, with a total weight loss corresponding to the weight of ligand without one atom of oxygen (obsd. 80.7, calcd. 80.4 %). The thermal decomposition behaviour of the complex corresponds to square planar geometry for monomeric unit of the complex. The weight loss from $200\text{--}248\text{ }^\circ\text{C}$ is believed to be due to the loss of the ligand, which is quite typical for organic-inorganic coordination polymers consisting of $\text{Cu}(\text{HFAC})_2$ cations and N,N' -bidentate-type ligands [17].

The first step weight loss of 9.5% in the Mn(II) complex within the temperature range $140\text{--}330\text{ }^\circ\text{C}$ correspond to loss of one carbon atom and two coordinated water molecules per repeated unit of polymer metal complex. The second weight loss has been observed in a single step within the temperature range of $330\text{--}460\text{ }^\circ\text{C}$, which correspond to the decomposition of the ligand without one oxygen atom. The second weight loss was observed with Mn(II) complex giving finally its metal oxide. Thus, weight loss behaviour has given an indication for octahedral geometry for monomeric unit of the complex.

3.4 Catalytic activity test

The liquid phase catalytic hydroxylation of phenol using synthesized catalysts viz. $[-\text{CH}_2\{\text{Cu}(\text{bis-salan})\}_n]$ and $[-\text{CH}_2\{\text{Mn}(\text{bis-salan})\}_n \cdot 2\text{H}_2\text{O}]$ was studied as a function of time with H_2O_2 as an oxidant. The main products of phenol hydroxylation using H_2O_2 were catechol and hydroquinone and no other products were detected. The oxidation of phenol without catalyst was very slow ($< 1\%$).

The optimized reaction conditions were studied through variation of reaction parameters such as temperature, time, type of oxidants and solvents, volume of solvent, amount of catalyst and phenol to H_2O_2 molar ratio.

The performance of these catalysts has been found to be dependant on several factors such as amount of oxidant, catalyst, volume and type of solvent and temperature of the reaction mixture. The conditions for hydroxylation of phenol were optimized using H_2O_2 as an oxidant (5.67g H_2O_2 ; 4.7 g phenol; 0.01 g catalyst in 2 ml acetonitrile at $80\text{ }^\circ\text{C}$). Under optimized reaction conditions, the activity for Cu-based catalysts is more active than Mn-based catalyst at 6 h reaction time (Fig. 1). It has also been observed that catechol formation was always higher than hydroquinone formation. However, the conversion of phenol was at the expense of selectivity for the formation of catechol (Fig. 2).

On comparing the catalytic data found herein with the data reported in literature, it is clear that these coordination polymers are better catalysts than TS-2 [18] but lower than TS-1 [2] catalyst. However, the selectivity of the Mn-based catalyst towards catechol formation is superior to that of TS-1 and TS-2. Cu-based catalyst shows comparable or higher activity than various metal encapsulated zeolite-Y [10-11]. These coordinated polymers were more active than the related neat complexes in homogeneous medium as it was found in $[-\text{CH}_2\{\text{M}(\text{sal-1,2-pn})\}_n]$. From these results, it

has also been concluded that the nature of the central metal ion in the catalyst has a marked effect on phenol conversion and product selectivity.

The recycled catalysts have exhibited almost similar catalytic activity due to the stability of the catalysts and were confirmed by recording IR spectra.

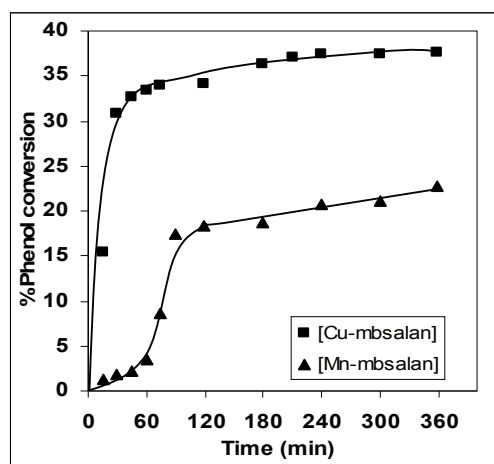


Fig. 1: % Phenol conversion

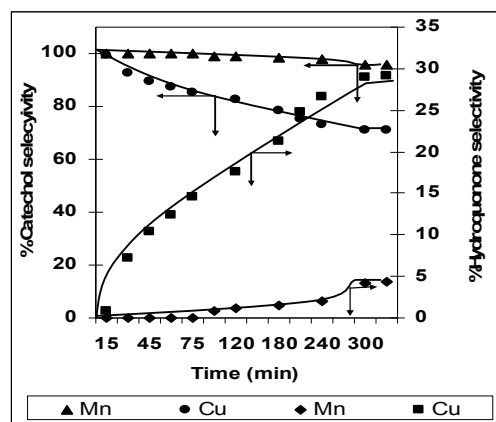


Fig. 2: % CAT/HQ selectivity

4 CONCLUSION

Two coordination polymers derived from Schiff base ligand 5,5'-methylene bis(salicylidene)aniline with two different metal ions have been synthesized and characterized by various physico-chemical techniques. These catalysts show potential catalytic activity for hydroxylation of phenol. The optimized conditions for hydroxylation of phenol were using H_2O_2 as oxidants are (5.67g H_2O_2 ; 4.7 g phenol; 0.01 g catalyst in 2 ml acetonitrile at $80^\circ C$).

The Cu-based catalyst shows higher activity than the Mn-based catalysts. While Mn-based catalyst shows a much higher selectivity to catechol (~96%) than the Cu-based catalyst (~71%).

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