

Environmentally benign catalytic hydroxylation of benzene using metal coordination polymers

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ABSTRACT

Environmentally benign synthetic processes of phenol from benzene via single step by using new two metal-Schiff-base coordination polymer. These catalysts were synthesized and characterized which are derived from the ligand bis-bidentate 5,5'-methylene-bis(*N*-methylsalicylidene-1,2-diaminopropane) (MBSP) and metal ions [Co(II) and Mo(VI)]. The catalytic activity of these catalysts towards the hydroxylation of benzene was evaluated under heterogeneous conditions using hydrogen peroxide as a green oxidant. Under the optimized conditions, the Co-based catalyst show good activity with excellent selectivity (100%) towards phenol. These catalysts were stable in hydroxylation of phenol and were reused after recovering with no significant loss in their catalytic activity.

Keywords: green oxidant, metal-coordination polymers, benzene hydroxylation

1 INTRODUCTION

Phenol is known to be one of the most important intermediate for the synthesis of various products ranging from plastics to petrochemicals and agrochemicals. Commercial phenol production is mainly based on three-step cumene process [1] from benzene and propylene. However, this process results in a low phenol yield and is highly energy-consuming. Therefore, much effort has been devoted to develop new processes to produce phenol in one-step which is economically and environmentally favorable without by-products, with a high selectivity and under mildest conditions.

In the bulk chemical industry, classical processes are environmentally unacceptable, non-selective and thus have been largely supplemented by cleaner alternate catalysts. For these reasons, to develop alternative oxidation processes based in a green and non-toxic oxidant is one of the main challenges to overcome by chemical industry. Hydrogen peroxide is a great green chemistry reactant as it degrades into water and oxygen as the only by-products. Accordingly, the direct hydroxylation of benzene to phenol has become one of the most challenging from economical

and environmental viewpoint [2–5]. Moreover, various heterogeneous catalysts have been studied for this reaction using hydrogen peroxide as a clean oxidant [6–11].

As a continuation of research on catalyzed hydroxylation of benzene [12], we describe the synthesis of new two Schiff-base coordination polymers derived from the ligand bis-bidentate 5,5'-methylene-bis(*N*-methylsalicylidene-1,2-diaminopropane) (MBSP) and metal ions Co(II) and Mo(VI). The coordination polymers were characterized by various physico-chemical techniques. These synthesized polymers were screened as heterogeneous catalysts for the liquid phase hydroxylation of benzene using H₂O₂ as an oxidant. The optimized reaction conditions were studied such as temperature, time, amount of catalyst and substrate to H₂O₂ molar ratio.

2 EXPERIMENTAL

2.1 Materials

All chemicals and solvents were of AR grade and used without purification. [MoO₂(acac)₂] was prepared following the literature procedure [13].

2.2 Physical methods and analyses

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 elemental analyses were performed at Elemental Analyzer CHN Thermo. The metal content was measured by using GBC Avanta atomic absorption spectrophotometer. Thermal studies were carried out on Perkin Elmer Pyris Diamond TG/DTA. The magnetic susceptibility measurement was carried by Gouy method. 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 0.5μm film thickness). 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.

2.3 Catalysts Preparation

2.3.1 Synthesis of 5,5'-methylene bis(salicylaldehyde)

5,5'-methylene bis(salicylaldehyde) was prepared following the method of Marvel and Tarkoy [14] with slight modification.

2.3.2 Synthesis of polymeric ligand, *N,N'*-bis-[5,5'-methylenesalicylidene]-1,2-diaminopropane, [-CH₂(H₂sal-1,2-pn)-]_n, (MBSP)

5,5'-Methylenebis(salicylaldehyde) (2.56 g, 0.01 mol) was dissolved in 20 ml methanol. To this solution was added a methanolic solution of 1,2-diaminopropane (0.74 g, 0.01 mol in 10 ml) dropwise with continuous stirring and the reaction mixture was refluxed for 2 h. The obtained yellow solid mass was filtered, washed with methanol. The crude mass was purified by refluxing in methanol, filtered and dried at ca. 100 °C in air oven.

2.3.3 Synthesis of metal coordinated complexes

2.3.3.1 [-CH₂{Co(sal-1,2-pn).2DMF}-]_n

The Co-coordinated complex was prepared by adding (0.5 g, 0.002 mol equivalent of repeating unit) of the polymeric ligand [-CH₂(H₂sal-1,2-pn)-]_n MBSP in DMF (10 ml) to Co(II) acetate (0.002 mol) in 10 ml DMF. The coloured solution obtained was brought to digest on water bath for 2 h. A reddish-brown precipitate was formed and the solid obtained in each case was filtered, washed with hot DMF, refluxed with methanol for 1 h to purify the crude mass, and dried at 120 °C.

2.3.3.2 [-CH₂{MoO₂(sal-1,2-pn)}-]_n

The ligand [-CH₂(H₂sal-1,2-pn)-]_n (0.50 g, 0.002 mol equivalent of repeating unit) was dissolved in 10 ml of DMF by heating at ca. 90 °C and to this [MoO₂(acac)₂] (0.66 g, 0.002 mol) was added in one portion with stirring. The obtained reaction mixture was digested on a water bath for 2 h. After reducing the volume of the solvent to ca. 10 ml, the same amount of methanol was added and solution was kept in refrigerator for over night. The separated orange solid was filtered, washed with methanol and dried at 120 °C.

2.4 Catalytic activity test

The liquid phase catalytic hydroxylation of benzene using 30% H₂O₂ solution as an oxidant was performed

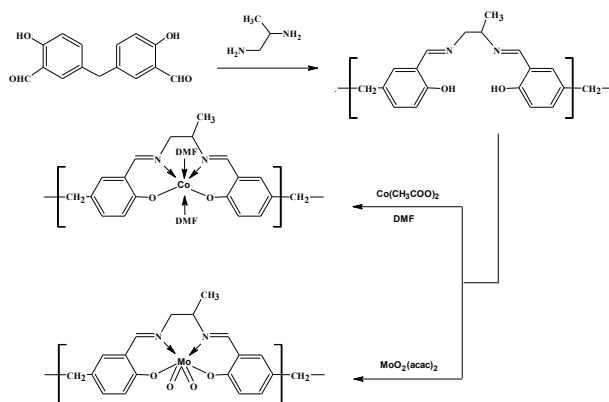
under atmospheric pressure in a two-necked round bottomed flask equipped with a water condenser, magnetic stirrer. A mixture of benzene (1.56 g, 0.02 mol), and 30% H₂O₂ (2.36 g, 0.02 mol) in 2 ml acetonitrile as solvent was kept in the flask and heated to 70 °C under vigorous stirring. After attainment of temperature, catalyst (0.01 g) was added to the reaction mixture and reaction was followed just after addition of the catalyst. At pre-determined time intervals, the samples were withdrawn from the reaction mixture and analyzed through gas chromatograph. The effect of various parameters, such as, reaction time, temperature, amount of catalyst and oxidant, and volume of solvent, on benzene oxidation was studied.

3 RESULTS AND DISCUSSION

3.1 Synthesis of catalysts

The polymeric ligand (MBSP) was formed by condensation of equimolar ratio of 5,5'-methylene bis(salicylaldehyde) with 1,2-diaminopropane in methanol. The reaction of Co(II) acetate and [MoO₂(acac)₂] with the Schiff base ligand [-CH₂(sal-1,2-pn)-]_n proceed smoothly in hot DMF in a 1:1 ratio affording the corresponding coordinated complexes as shown in Scheme 1. These complexes are insoluble in all coordinating non-coordinating solvents that confirm it polymeric nature,

The proposed structures of these catalysts were confirmed by elemental analyses, spectroscopic, magnetic measurements and thermal analysis.



Scheme 1: Synthetic route of the catalysts

3.2 Characterization of catalysts

3.2.1 Spectral analyses

These catalysts are characterized by IR spectroscopy. In accordance with structure of the ligand (MBSP), a broad band of medium intensity appeared between 2400-2700 cm⁻¹ due to hydrogen bonding between phenolic hydrogen and azomethine nitrogen. This band has disappeared on

complexation with metal ions, which indicates the coordination of phenolic oxygen to the metal ion after deprotonation. A multiple bands centred at 2960 cm^{-1} is attributed to CH_2 group. These bands are also found in all metal complexes at around the same position, which indicated that methylene group remained undisturbed after complexation. The ligand exhibits a sharp $\text{C}=\text{N}$ band at 1635 cm^{-1} , which on complexation is shifted to lower frequency by $4\text{-}13\text{ cm}^{-1}$. This shift has indicated the coordination of metal ions with azomethine nitrogen. The complexation is also confirmed by the appearance of new bands at $422\text{-}433$ and $471\text{-}523\text{ cm}^{-1}$ due to $\nu(\text{M-N})$ and $\nu(\text{M-O})$, respectively. Thus, each unit of polymeric ligand behaved as dibasic tetradentate ONNO donor.

In Co-complex an additional band at $\sim 1640\text{ cm}^{-1}$ corresponding to $\nu\text{ C}=\text{O}$ stretching was due to coordination of oxygen of DMF with metal ions. The free DMF exhibits $\nu\text{ C}=\text{O}$ band at 1680 cm^{-1} , which has lowered by $20\text{-}25\text{ cm}^{-1}$ on complexation. This is further evidence for the coordination of DMF with cobalt ion through its oxygen. The dioxomolybdenum complex has exhibited two sharp bands at 915 and 885 cm^{-1} , which are within the range as found (ν_{sym} , $892\text{-}964$; ν_{asym} $840\text{-}925\text{ cm}^{-1}$) with reported *cis*-dioxo Mo(VI) complexes [15].

The electronic spectrum of the polymeric ligand has shown two bands at $239, 307\text{ nm}$ due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. These bands were shifted to lower frequency, indicating the coordination of metal ions with azomethine nitrogen of the ligand. The Co(II) complex has shown one new band at 424 nm , which is assigned for ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})\nu_3$ transitions [16].

Dioxomolybdenum (VI) complex display one band at 418 nm , which is attributed to Ligand \rightarrow Metal Charge transfer (LMCT).

3.2.2 Thermogravimetric analysis

Thermogram of $[-\text{CH}_2\{\text{Co}(\text{sal-1,2-pn})_2\text{DMF}\}]_n$ indicates weight loss corresponding to two DMF molecules per repeated unit of polymer metal complex. This weight loss between temperature range $150\text{-}290\text{ }^\circ\text{C}$ indicated the presence of DMF molecules as labile ligand. The simultaneous decomposition of methylene group and two molecules of DMF are responsible for higher weight loss in these complexes. The observed weight loss theoretically corresponds to the removal of two molecules of DMF and one carbon atom in each case. The thermogravimetric analysis has been recorded under atmospheric conditions; hence carbon has been removed as carbon dioxide. Further decomposition has shown on increasing the temperature beyond $260\text{ }^\circ\text{C}$ corresponds to the weight loss of complete ligand without one atom of oxygen.

The $[-\text{CH}_2\{\text{MoO}_2(\text{sal-1,2-pn})\}]_n$ complex is anhydrous in nature as this complex does not show any weight loss up to $200\text{ }^\circ\text{C}$. However, a weight loss equivalent to one carbon atom per repeating unit of polymeric complexes was observed above this temperature ($> 200\text{ }^\circ\text{C}$), which

confirmed the breaking of the chelating polymeric repeating unit as observed above. The second step shows continuous weight loss due to the decomposition of remaining ligand carbon skeleton of polymeric repeating unit until the formation of metal oxide. The residual weight after decomposition corresponds to the calculated weight of molybdenum oxide. Thus, on the basis of thermogravimetric behaviour of these complexes, an octahedral geometry has been proposed for monomeric unit of $[-\text{CH}_2\{\text{Co}(\text{sal-1,2-pn})_2\text{DMF}\}]_n$ and dioxomolybdenum (VI) complexes.

3.3 Catalytic activity test

The liquid phase hydroxylation of benzene using 30% H_2O_2 as an oxidant catalyzed by the synthesized metal coordination polymers gave only one product, i.e. phenol.

The effect of different reaction conditions on hydroxylation of benzene has been studied in detail using $[-\text{CH}_2\{\text{Co}(\text{sal-1,2-pn})_2\text{DMF}\}]_n$, which enabled suitable reaction conditions for maximum transformation of benzene as well as better selectivity for the formation of phenol. The results of hydroxylation of benzene over these catalysts are presented in Table 1.

Using 5.0 mg of catalyst $[-\text{CH}_2\{\text{Co}(\text{salpn})_2\text{DMF}\}]_n$ for the fixed amount of benzene (1.56 g) and aqueous 30% H_2O_2 (2.36 g) in 2 ml MeCN, only about 11% of benzene oxidation was achieved at $70\text{ }^\circ\text{C}$ in 6 h of reaction time. However, increment of catalyst amount to 10.0 mg showed significant change and conversion reached to 15.3% . Further increment of catalyst hardly improves the conversion.

Similarly, running the reaction at various temperatures while keeping the optimized conditions fixed i.e amount of benzene and H_2O_2 and catalyst (10.0 mg) in 2 ml of MeCN has shown considerable effect on the oxidation of benzene. As shown in Table 1, at least $70\text{ }^\circ\text{C}$ is the required temperature to supply sufficient energy to reach the energy barrier of benzene transformation.

The volume of solvent also influences the rate of the reaction. Increasing the volume of solvent, the catalytic reaction always led to the poor performance. Reaction at 2 ml of acetonitrile was found to be sufficient for maximum conversion of benzene. The activity of catalyst was poor in absence of solvent, which may due to inhomogenation of the reaction mixture.

The effect of H_2O_2 concentration was studied using three different molar ratios of H_2O_2 :benzene. The results indicate that H_2O_2 /benzene molar ratio of $1:1$ is ideal ratio to get maximum conversion as well as maximum efficiency. Thus large concentration of oxidant is not an essential condition to maximize phenol conversion.

Fig. 1 shows the oxidation of benzene using Co-based catalyst proceeds rapidly during the first 2 h and reached to maximum of 15% conversion, in 6 h . Thereafter, only a very slow conversion was observed up to 24 h .

Comparing the activity of our catalysts for hydroxylation of benzene to the literature data; Fe-Al-SBA-15 [17], Cu-

ZSM-5 [18] and modified TS-1 [19], however, Co-MBSP catalyst shows higher activity.

Table 1: Catalytic activity over Co-MBSP

Reaction parameters	Reaction Conditions	% Benzene conversion	% Selectivity (phenol)	TOF ^a (h ⁻¹)
Reaction temperature (°C)	50	5.8	100	9.6
	60	9.5	100	16
	70	15.3	100	25
Amount of catalyst	5 mg	10.96	100	36
	10mg	15.30	100	25
	25mg	16.11	100	11
H ₂ O ₂ :benzene (molar ratio)	0.5:1	9.9	98.9	33 (16)
	1:1	15.3	100	25 (13)
	2:1	17.2	100	5 (7)
Volume of solvent	2ml	15.3	100	25
	4ml	10.7	100	34
	6ml	6.1	100	10.1

Reaction conditions: Benzene (0.02 mol); solvent, CH₃CN; catalyst [CH₂{Co(sal-1,2-pn).2DMF}-]_n; time = 6 h.

a) TOF Turn over frequency: moles of substrate converted per mole of metal (in the solid catalyst) per hour.

b) The data in the parenthesis represent the H₂O₂ efficiency (%) = (moles of H₂O₂ utilized in products formation/moles of H₂O₂ added) x 100.

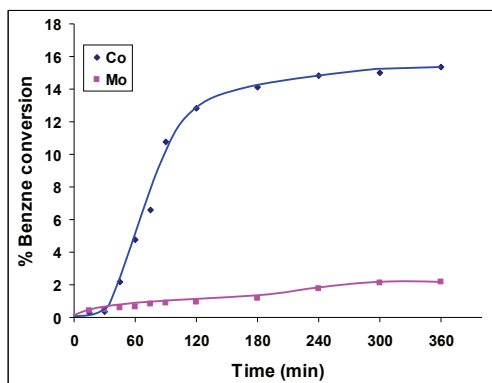


Fig. 1: % Benzene conversion with time over both catalysts

4 CONCLUSION

Coordinated metal complexes of polymeric ligand [-CH₂(H₂sal-1,2-pn)-]_n with Co(II) and Mo(VI) metal ions have been synthesized and characterized.

On the basis of Chemical analyses, spectroscopic studies and magnetic measurements as well as thermogravimetric analyses of these complexes, an octahedral geometry has been proposed for monomeric unit of cobalt (II) and dioxomolybdenum (VI) complexes.

The catalytic activity of Co-MBSP catalyst is higher than the Mo-MBSP. On the other hand, both catalysts show excellent selectivity towards phenol (100 %) under the optimum reaction conditions (0.02 mol of benzene, 0.02 mol of H₂O₂ and 0.010 g of catalyst at 70 °C).

These catalysts systems can be recovered and reused without particular loss of activity. This study would be valuable in developing a new environmentally benign route for phenol synthesis.

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