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Transition metal coordination polymers: Synthesis and catalytic study for hydroxylation of phenol and benzene

Hanna S. Abbo*, Salam J.J. Titinchi

Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, Cape Town, South Africa

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ABSTRACT

New coordination polymers of Ni(II) and Cu(II) of the polymeric salen-type Schiff base ligand derived from the condensation of 5,5′-methylene bis-(salicyaldehyde) with 1,2-diaminopropane yielded *N*,*N*′-1,2-propylenebis(5-methylenesalicylidenamine) abbreviated $[-CH_2(H_2sal\text{-}1,2\text{-}pn)-]_n$ have been synthesized. Both coordinated polymers with the general formula of $[-CH_2(ML{\cdot}XDMF)-]_n$, where X = 0, M = Cu; *N*,*N*′-1,2-propylenebis(5-methylenesalicylidenaminato)copper(II) and X = 2, M = Ni; *N*,*N*′-1,2-propylenebis(5-methylenesalicylidenaminato)nickel(II) have been characterized by elemental analysis, magnetic susceptibility measurements, IR, electronic spectra and thermogravimetric studies. The ligand behaves as a bis-bidentate molecule coordinating through the phenolic oxygen and azomethine nitrogen atoms.

These coordinated polymers have been assessed as catalysts for liquid phase hydroxylation of phenol and benzene using H_2O_2 as an oxidant. The results show a high activity and selectivity of both catalysts toward the formation of diphenols from phenol, and a low activity in the oxidation of benzene. The Cu-based catalyst exhibited higher activity than Ni-based catalyst for hydroxylation of phenol and benzene. The activity and efficiency of H_2O_2 depends on the reaction parameters *viz.*, temperature, molar ratio of the reactants and the solvent. Concentration of the oxidant and other reaction parameters has been optimised for the maximum oxidation of these substrates. These catalysts can be recovered and reused without notable loss of activity.

1. Introduction

Production of phenol and diphenols from the hydroxylation of aromatic compounds is an important industrial application. Therefore, much attention has been focused on their production through catalytic routes, in particular direct hydroxylation of benzene and phenol by H_2O_2 [1]. Hydrogen peroxide which has high active oxygen content has been widely explored as a green oxidant in oxidation reactions, because it is readily available and the resulting by-products (water and molecular oxygen) are environmentally friendly. Hydroxylation of phenol usually produces catechol and hydroquinone which are used in industrial syntheses as antioxidants, polymerization inhibitors, photographic chemicals and fine chemical industries [2,3]. Mineral acids, simple metal ions and transition metal-based complexes are well-known traditional catalysts for the hydroxylation of phenol [4]. Metal ion-exchanged or supported on zeolites, hydrotalcites, and resins [5–11] have been increasingly studied in order to overcome the disadvantage of homogeneous catalysts *viz.*, recovery and reuse of the catalyst. TS-1 was revealed to be novel and the most highly efficient heterogeneous catalyst (Enichem) in this area [12]. To date, many researchers have been interested in the development of heterogeneous catalysts which are more active than TS-1 for hydroxylation of phenol, but most of them suffer from leaching of the active metal in the liquid phase and behave as homogeneous rather than heterogeneous catalysts [13].

On the other hand, phenol is mainly manufactured by a three-step cumene process, and has many disadvantages such as low yield, high energy consumption and production of an equal amount of acetone as the by-product [14]. Hence, finding alternative ways to produce phenol that overcome the disadvantages of the current cumene process has become one of the most challenging tasks in oxidation catalysis from an economical and environmental viewpoint. Direct hydroxylation of benzene to produce phenol is performed both in the liquid and gas phase. Direct hydroxylation of benzene is mainly focused on three preparation routes using the oxidants nitrous oxide [15–18], hydrogen peroxide [6,19,20], and molecular oxygen [21]. Moreover, various heterogeneous catalysts have been studied for this reaction [22]. Currently, transition metal coordination polymers have found increasing interest due to their possible technological and industrial applications such as separation, ion-exchange and catalysis. Coordination polymers,

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* Corresponding author. Tel.: +27 21 959 2217; fax: +27 21 959 3055.
E-mail address: habbo@uwc.ac.za (H.S. Abbo).

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i.e. polymeric metal complexes derived from polymeric chelating ligands showed remarkable thermal stability and since they are insoluble in common solvents, acted as heterogeneous catalysts in the oxidation reactions [23–26].

Continuing our research on the hydroxylation of phenol and benzene through the catalytic route; we wish to report on the synthesis of new coordination polymers derived from bis-bidentate, *N,N*′-1,2-propylenebis(5-methylenesalicylidenamine) and the metal ions, Cu(II) and Ni(II). Their chemical structures are shown in Scheme 1. The coordination polymers were characterized by various physico-chemical techniques. These coordination polymers were screened as catalysts for the liquid-phase hydroxylation of phenol and benzene with 30% H_2O_2. Optimum reaction conditions were investigated and are discussed.

2. Experimental

2.1. Materials, physical methods and analyses

All chemicals and solvents were of AR grade and used without purification. 5,5′-Methylene bis(salicylaldehyde) [27] was prepared following the literature procedures. Elemental analyses of ligands and metal complexes were determined by Carlo Erba 1108. The metal content was measured by using GBC Avanta atomic absorption spectrophotometer. Magnetic susceptibility measurements were made on Gouy's balance at room temperature with $Hg[Co(SCN)_4]$ as a calibrant and the diamagnetic corrections were made using Pascal's constant. Infrared spectra were recorded in KBr on a PerkinElmer model 1600 FT-IR spectrophotometer. Electronic spectra were recorded in Nujol on a PerkinElmer Lambda 35 UV/VIS spectrophotometer by layering mull of the sample to the inside of one of the cuvette while keeping the other cuvette layered with pure nujol as reference. ^{1}H NMR spectra were recorded in $CDCl_3$ + 2 drops DMSO-d_6 using a Varian XR200 spectrometer. Sample signals are relative to the resonance of residual protons on carbons in the solvent. A LEO 435 VP model was used for Scanning Electron Microscope (SEM). Thermal studies were carried out on PerkinElmer Pyris Diamond TG/DTA under atmospheric air. Reaction products were analyzed using gas chromatograph HP 5890 fitted with FID detector and 10 m × 0.53 (i.d.) and hp1 capillary column.

2.2. Preparations

2.2.1. Synthesis of 5,5′-methylene bis(salicylaldehyde)

Salicylaldehyde was converted to 5,5′-methylene bis-(salicylaldehyde) by the classical methylation method as shown in Scheme 1.

2.2.2. Synthesis of *N,N*′-1,2-propylenebis(5-methylenesalicylidenamine) polymeric ligand, $[-CH_2(H_2sal\text{-}1,2\text{-}pn)-]_n$

The polymeric ligand was prepared by adding dropwise equimolar amount of a methanolic solution of 1,2-diaminopropane (0.74 g, 0.01 mol) in 10 ml, to a hot methanolic solution of MBSal (2.56 g, 0.01 mol) in 30 ml. The reaction mixture was refluxed for 2 h, the separated solid was filtered and purified by refluxing with methanol for 2 h. The yellow solid obtained was dried at ambient temperature. Yield 72%, m.p. 180–184 d. Anal. Found: C, 73.2; H, 6.0; N, 9.6. $C_{18}H_{18}N_2O_2$ requires C, 73.4; H, 6.1; N, 9.5%.

2.2.3. Synthesis of coordinated metal complexes

The coordinated polymers were prepared by dissolving (0.002 mol equivalent of repeating unit) of the ligand $[-CH_2(H_2sal\text{-}1,2\text{-}pn)-]_n$ in 10 ml of dimethyl formamide (DMF) at 90 °C. To this solution, the respective metal acetate [M = Cu(II) and Ni(II)] (0.002 mol) dissolved in 10 ml of DMF were added. The colored solution obtained in each case was digested on a water bath for 2 h. A blackish-green precipitate was formed in the case of the Cu-complex, whereas no precipitate was formed for the nickel complex. The Ni-complex was obtained as a brown solid by adding methanol to the reaction mixture and kept overnight at 5 °C. The solids were filtered, washed with DMF followed by methanol. The crude solids were purified by refluxing with methanol for 1 h and dried at 120 °C.

N,N′-1,2-propylenebis(5-methylenesalicylidenaminato)copper (II); $[-CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}-]_n$, yield: 58%, m.p. >300 °C; Anal. Found: C, 60.9; H, 4.5; N, 8.2; Cu, 17.6. $C_{18}H_{16}N_2O_2Cu$, requires C, 60.8; H, 4.5; N, 7.9, Cu; 17.9%. μ_{eff} = 1.9 BM

N,N′-1,2-propylenebis(5-methylenesalicylidenaminato)nickel (II)·2DMF; $[-CH_2\{Ni(sal\text{-}1,2\text{-}pn)\cdot 2DMF\}]_n$, yield: 42%, m.p. >300 °C. Anal. Found: C, 58.2; H, 6.1; N, 11.1; Ni, 11.5. $C_{24}H_{30}N_4O_4Ni$, requires C, 58.0; H, 6.0; N, 11.3, Ni; 11.8%, μ_{eff} = 3.3 BM

2.3. Catalytic activity test

The catalytic hydroxylation of phenol and benzene using 30% H_2O_2 solution as an oxidant was carried out in a two-necked round bottom flask fitted with a water condenser and immersed in a thermostated oil bath that was maintained at different preset temperatures.

In a typical hydroxylation process, a mixture of substrate and 30% H_2O_2 in a chosen solvent was warmed to the desired temperature. To this mixture the catalyst was added to start the reaction. The reaction mixture was continuously stirred for the prescribed time. Each experiment was reproduced at least 2 or 3 times. Samples were periodically withdrawn during reaction, filtered and analyzed by gas chromatograph (2 μl diluted with 1 ml H_2O and extracted with chloroform). After the reactions, catalysts were filtered off, regenerated by Soxhlet extraction with acetonitrile and dried at 120 °C for 6 h, and then reused.

3. Results and discussion

3.1. Characterization

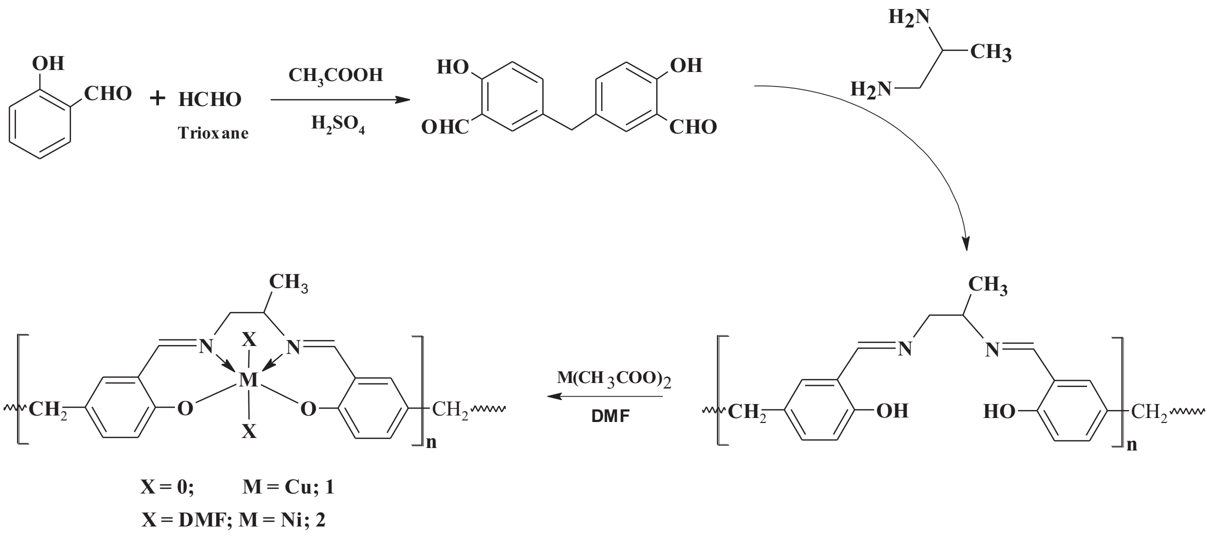
The polymeric ligand was synthesized by the condensation of equimolar of 5,5′-methylene bis-(salicyaldehyde) with 1,2-diamino-propane as shown in Scheme 1.

The ^{1}H NMR spectral data (δ in ppm) of the polymeric ligand $[-CH_2(H_2sal\text{-}1,2\text{-}pn)-]_n$ are as follow; broad band at 13.15 (br, 2H, OH), two sharp peaks at 8.24 (s, 1H, $-CH{=}N-$) and at 8.28 (s, 1H, $-CH{=}N-$) are assigned to non-equivalent azomethine protons of different environment, 6.77–7.36 (m, 6H, aromatic). An unresolved multiplet band ranging from 3.49 to 4.04 (m, 3H, $-CH_2$ (isopropyl) and $-CH-$ (isopropyl)) having a singlet at δ 3.68 (s, 2H, CH_2 (bridging methylene)) was also shown by the repeating unit. A well resolved doublet with 1:1 intensity ranging from 1.37 to 1.39 (d, 3H, methyl isopropyl group) has been developed due to the coupling of methine and methyl protons of the isopropyl group. In view of observed peaks in ^{1}H NMR spectrum of the repeating unit, the structure of the repeating unit is confirmed.

The metal complexes are colored and insoluble in most coordinating and non-coordinating solvents that confirm its polymeric nature. Elemental and metal analyses support the formation of complexes and the presence of metal ions in each pocket of coordinating atoms as proposed.

3.1.1. IR spectral studies

In accordance with structure of the ligand $[-CH_2(H_2sal\text{-}1,2\text{-}pn)-]_n$, a broad band of medium intensity appeared in the frequency range of 2400–2700 cm^{-1} due to hydrogen bonding between phenolic hydrogen and azomethine nitrogen. This band



Scheme 1. Synthetic route for the coordination polymers.

disappeared on complexation with metal ions, which indicates the coordination of phenolic oxygen to the metal ion after deprotonation. This is further supported by the fact that new bands appeared between 471 and 521 cm^{-1} on complexation with metal ions, which has been attributed to ν(M—O) vibrations.

Multiple bands centred at 2960 cm^{-1} in the ligand spectra 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 with metal ions. Sharp C=N absorption band at 1635 cm^{-1} was found in the spectrum of the ligand, which on complexation with metal ions shifted to lower frequency by 10–13 cm^{-1}. This shift in the peak suggested the coordination of metal ions with the nitrogen of the azomethine group, which is also confirmed by the appearance of new bands within the frequency of ~432 cm^{-1} due to ν(M—N) vibrations [28]. Thus, each unit of polymeric ligand behaves as dibasic tetradentate ONNO donor.

In the Ni complex an additional band at ~1640 cm^{-1} corresponding to ν(C=O) was observed due to coordination of the oxygen of DMF with metal ions. The free DMF exhibits the ν(C=O) band at 1680 cm^{-1}, but on complexation with metal ions is lowered by 20–25 cm^{-1}, which further provided evidence for the coordination of DMF with metal ions through its oxygen [29].

3.1.2. Electronic spectral studies

The electronic spectra of the polymeric ligand [—CH$_2$(H$_2$sal-1,2-pn)—]$_n$ had two bands at 239 and 307 nm due to $\pi \to \pi^*$ and $n \to \pi^*$ transitions, respectively (Fig. 1). These bands were shifted to lower energy indicating the coordination between metal ions and the azomethine nitrogen of the ligand. The Ni (II) complex has one new band at 429 nm, which is assigned to the $^3A_{2g} \to {}^3T_{1g}$ (P) ν_3 transitions along with a band at 462 nm corresponding to the $^1A_{1g} \to {}^1T_{2g}$ transition as shown by most of the metal complexes [30]. The electronic spectrum of [—CH$_2${Cu(sal-1,2-pn)}—]$_n$ exhibits two bands at 395 and 561 nm. The latter band is assigned to the *d*–*d* transition, while the former one is due to a symmetry forbidden ligand → metal charge transfer (LMCT) transition similar to that observed in Cu(CH$_3$COO)$_2$(H$_2$O) at 370 nm [31]. Other bands appearing at 261 and 287 nm are assigned as intra-ligand transitions.

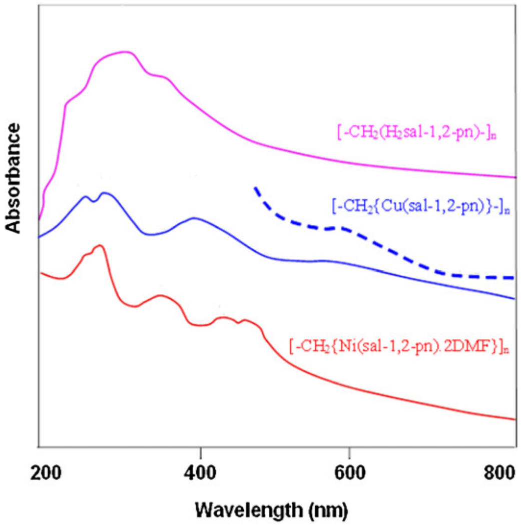


Fig. 1. Electronic spectra of the polymeric ligand and its metal complexes.

Table 1
Thermogravimetric analysis data for polymeric ligand and its metal complexes.

Repeating unit ligand/complex	Temp. range (°C)	% wt. loss obsd. (calcd.)	Group decomposed	Residue of ligand/complex	Final wt. residue obsd. (calcd.)
[—CH$_2$(H$_2$sal-1,2-pn)—]$_n$	130–170	5.0 (4.8)	C	[H$_2$sal-1,2-pn]	
	170–530	95.0 (95.2)	L-C	–	–
[—CH$_2${Cu(sal-1,2-pn)}—]$_n$	200–255	3.1 (3.4)	C	[Cu(sal-1,2-pn)]	22.60 (22.4)
	255–570	74.3 (74.2)	L-(C + O)	CuO	14.85 (15.04)
[—CH$_2${Ni(sal-1,2-pn)·2DMF}—]$_n$	180–260	31.74 (31.81)	C + 2DMF	[Ni(sal-1,2-pn)]	
	360–540	53.41 (53.15)	L-(C + O)	NiO	

3.1.3. *Thermal analysis*

The TGA data of the polymeric metal complexes along with their parent polymeric ligand for comparison are given in Table 1. Thermogram of the Ni-complex indicates weight loss corresponding to two DMF molecules per repeating unit of polymer metal complex. This weight loss between 150 and 290 °C indicated the presence of DMF molecules as being the labile ligand. The simultaneous decomposition of the methylene group and two molecules of DMF are responsible for the 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 (Table 1). The thermogravimetric analysis has been recorded under atmospheric conditions; hence carbon has been removed as carbon dioxide [24]. The Ni(II) complex decomposed further on increasing the temperature beyond 260 °C. The last decomposed fragment corresponds to the weight loss of a complete ligand without the oxygen atom because one atom of oxygen is retained by the metal ion in the formation of the metal oxide at high temperature (>540 °C).

The Cu-complex is anhydrous in nature and does not show any weight loss up to 200 °C. However, a weight loss equivalent of one carbon atom per repeating unit of polymeric complex was observed above 200 °C, which confirmed breaking of the chelating polymeric repeating unit. The second step of the thermogram shows continuous weight loss due to the decomposition of the remaining ligand carbon skeleton of polymeric repeating units until the formation of metal oxide. The residual weight after decomposition corresponds to the calculated weight of copper oxide.

Thus, on the basis of the thermogravimetric behavior of these complexes, an octahedral geometry has been proposed for the monomeric unit of the Ni-complex and square planer geometry for the Cu-complex, which is similar to other related complexes confirmed by X-ray crystal structure analysis [32,33]

The DTA curves of the complexes gave an indication of an exothermic reaction between 250 and 300 °C, which may be due to formation of carbon dioxide by decomposition of the methylene bridge. The second exothermic peaks is the DTA curves were due to formation of carbon dioxide and nitrogen oxides from the decomposition of remaining ligand of the monomeric repeating units of the complexes.

3.1.4. *Scanning electron microscopic*

The SEM micrograph of unmetalized polymeric ligand, Fig. 1S, indicated rough and porous surface with irregular shapes. This ligand on complexation with metal ions became compact, smoother and less porous due to coordination with metal ions which indicated the formation of the coordinated polymers.

3.2. *Catalytic activity*

3.2.1. *Hydroxylation of phenol*

Liquid phase hydroxylation of phenol catalyzed by these complexes using H_2O_2 as an oxidant has been studied in MeCN. Two major products, catechol and hydroquinone were identified by GC and no other oxidation product was detected from the reaction mixture with a mass balance of about 95%. The effect of catalyst concentration, temperature, solvent and phenol/H_2O_2 mole ratios on conversion profiles were examined in detail using the representative catalyst $[—CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}—]_n$ to optimize reaction conditions. Catalytic phenol hydroxylation does not occur in the absence of catalyst.

Table 2
Effect of catalyst weight on phenol hydroxylation[a].

Catal. wt (g)	PhOH/catal.[b]	% PhOH conv.[c] (6 h)	TOF (h^{-1})
0.005	3037	29	172
0.010	1708	48	142
0.025	683	51	60

[a] Reaction conditions: phenol (0.05 mol); phenol/H_2O_2 molar ratio = 1; solvent, CH_3CN (2 ml); catalyst $[—CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}—]_n$; reaction temperature 80 °C.

[b] Molar ratio per repeating unit.

[c] Phenol conversion (% mol).

TOF h^{-1}: Turn Over Frequency-moles of substrate converted per mole of metal (in solid catalyst) per hour.

Table 3
Effect of reaction temperature on % phenol conversion[a], product selectivity and Turn Over Frequency values.

Reaction temp. (°C)	%PhOH conv.	% Selectivity		TOF (h^{-1})
		Cat	HQ	
50	11.0	100	–	33
65	33.0	82.6	17.4	98
80	48.0	63.1	36.9	142

[a] Reaction conditions: phenol (0.05 mol); phenol/H_2O_2 molar ratio = 1; solvent, CH_3CN (2 ml); catalyst $[—CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}—]_n$, (10 mg); time = 6 h.

3.2.1.1. *Effect of catalyst amount.* Table 2 and Fig. 2S represent the effect of catalyst amount on activity and selectivity. Three amounts of catalyst *viz*., 5, 10 and 25 mg were used. Phenol conversion increases from 29 to 48% with increasing the amount of catalyst from 5 to 10 mg, which was achieved about 40% of total conversion in initial 1.5 h. However, increasing the amount of catalyst to 25 mg showed no significant effect on conversion (51%) and may be due to the fast decomposition of H_2O_2 in the reaction in the presence of an excess of catalyst. Therefore, the best molar ratio of phenol to the catalyst used is 1708 ideal for obtaining higher phenol conversion.

3.2.1.2. *Effect of reaction temperature.* The hydroxylation of phenol was carried out at three temperatures (50, 65 and 80 °C) keeping other parameters constant to optimized reaction temperature. It is observed that phenol conversion increases with temperature from 11 to 48% from 50 to 80 °C (Table 3, Fig. 3S). The reaction at 80 °C has an added advantage of achieving maximum conversion of phenol within 1.5 h of the reaction time. Selectivity towards catechol formation however decreases with increasing temperature. Therefore, the suitable temperature for this catalytic reaction is 80 °C.

3.2.1.3. *Effect of H_2O_2 concentration.* The reaction was carried out with varying amount of H_2O_2 to a fixed amount of phenol in (0.5:1, 1:1 and 2:1) H_2O_2: phenol molar ratios. As shown in Table 4 and Fig. 4S, maximum phenol conversion was obtained with molar ratios 2:1 and 1:1 (53.7 and 48.2%) respectively. It was more H_2O_2 efficient to run the reaction at 1:1 ratio (41%) than 2:1 ratio (24%). In fact, excess H_2O_2 is undesirable due to competing H_2O_2 decomposition, which keeps H_2O_2 to phenol ratios low. When the H_2O_2 is reduced to a 0.5:1 molar ratio, conversion decreased significantly to 19.1% with 33% H_2O_2 efficiency. The amount of *p*-benzoquinone formed

Table 4
Effect of H_2O_2: Phenol molar ratio on % phenol conversion[a] as a function of time over $[—CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}—]_n$.

H_2O_2:PhOH molar ratio	% PhOH conv.	% H_2O_2 eff.[b]	Product selectivity (%)		
			Cat.	HQ	BQ[c]
0.5:1	19.1	33	65.9	34.1	
1:1	48.2	41	63.1	36.9	
2:1	53.7	24	59.6	38.6	1.8

[a] Reaction conditions: Phenol (0.05 mol); catalyst $[—CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}—]_n$ (10 mg); solvent, CH_3CN (2 ml); reaction time = 6 h; reaction temperature 80 °C.

[b] % H_2O_2 efficiency = (moles of H_2O_2 utilized in products formation/moles of H_2O_2 added) × 100, (based on GC analysis data).

[c] *p*-Benzoquinone.

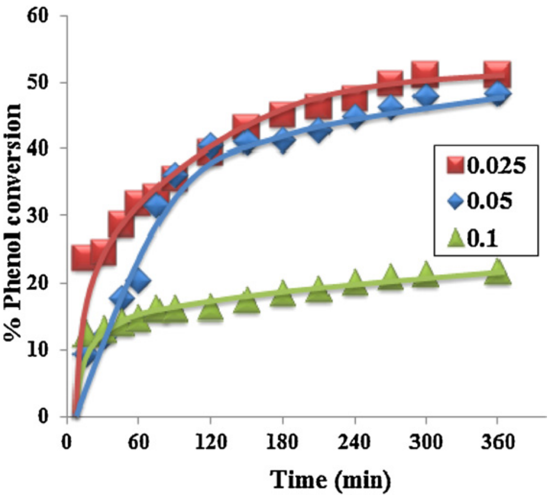


Fig. 2. Effect of phenol concentration on hydroxylation of phenol as a function of time catalyzed by [—CH_2{Cu(sal-1,2-pn)}—]$_n$.

at a molar ratio of H_2O_2 to phenol (2:1) was less than 2% due to the further oxidation of hydroquinone. However, product selectivity is similar in all cases. Taken collectively it is found that a 1:1 molar ratio is the most efficient to obtain maximum % conversion with reasonable H_2O_2 efficiency and high TOF value.

3.2.1.4. Effect of the oxidant. The reaction was carried out using oxidants other than H_2O_2, *viz.*, (70% aqueous) *tert*-butylhydroperoxide (TBHP) and sodium hypochlorite solution, NaOCl (available chlorine ≥4%). Phenol hydroxylation was by and large absent (less than *ca.* 2%) using these oxidants and is possibly due to the lack of generation of an active oxidant species and the solubility problems associated with the reactant *vis-à-vis* the oxidant which is in agreement with our results [25].

3.2.1.5. Effect of phenol concentration. The phenol concentration was varied in the reaction mixture from 0.025 to 0.1 mol keeping other parameters constant. It is clear from Fig. 2 that with 1:1 H_2O_2:PhOH molar ratio, a maximum of 48% overall conversion was obtained. When the phenol concentration to that of H_2O_2 was reduced to 1:0.5 molar ratio a maximum of 51% conversion was obtained. Increasing the amount of PhOH to twice of that of H_2O_2 resulted in the overall conversion to be reduced to 21%.

3.2.1.6. Effect of type of solvent. Many factors can influence reaction rates *viz.*, polarity, solvation power, donor ability, electrophilic behavior and molecule size of solvent. It is clear from Table 5 and Fig. 5S that acetonitrile is the best solvent with 48.2% conversion compared to other solvents used in this study. Although high catalytic activity was expected in nitrobenzene due its high polarity, it is clear from the data given in Table 5 that the percentage phenol conversion was low, which ultimately retarded the reaction rate since the reaction becomes viscosity controlled in nitrobenzene. The viscosity was increased due to formation of polymeric material. Similar observations were obtained with chloroform which is more polar than acetonitrile. It is clear that the type of solvent has a very significant role in controlling the overall % conversion of phenol which is not exclusively dependant on solvent polarity but hydrophilicity and solvent size may also explain the effect of selected solvents.

Table 5
Influence of various solvents on percentage phenol conversion[a], product selectivity, TOF and H_2O_2 efficiency after 6 h.

Solvent	PhOH conv. (%)	H_2O_2 eff. (%)	TOF (h^{-1})	Selectivity (%)	
				Cat	HQ
CH_3CN	48.2	41	142	63.1	36.9
MEK	36.5	31	108	68.4	31.6
n-Heptane	30.4	26	90	70.7	29.3
$PhNO_2$	21.9	19	65	72.3	27.7
$CHCl_3$	15.9	14	47	85.6	14.4

[a] Reaction conditions: Phenol (0.05 mol); phenol/H_2O_2 molar ratio = 1; catalyst [—CH_2{Cu(sal-1,2-pn)}—]$_n$ (10 mg); solvent (2 ml); reaction time = 6 h; at 80 °C; MEK, Methylethylketone.

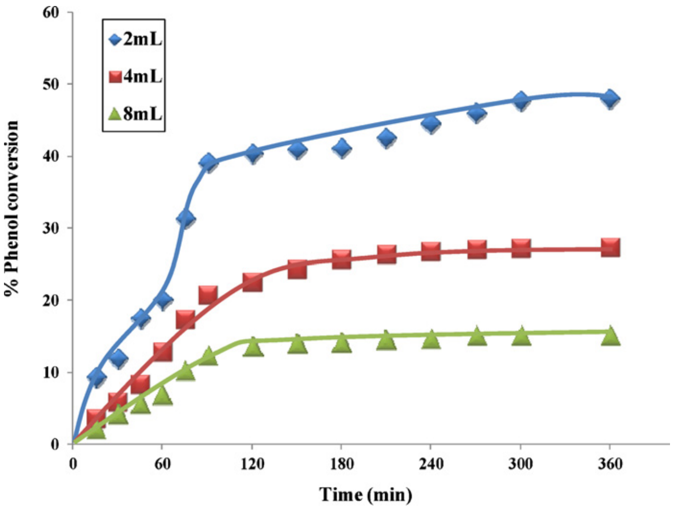


Fig. 3. Effect of volume of solvent (CH_3CN) on the hydroxylation of phenol as a function of time catalyzed by [—CH_2{Cu(sal-1,2-pn)}—]$_n$.

In terms of selectivity, using chloroform the reaction was found to be more selective towards catechol (85.6%) than the other solvents, but not as efficient as in acetonitrile.

3.2.1.7. Effect of volume of solvent. In order to study the influence of the volume of the reaction medium, the reaction was performed in various volume of solvent (CH_3CN). From Fig. 3, it can be concluded that the volume of acetonitrile used has a great role on the % conversion. Using 2 ml of MeCN was found to be sufficient to perform the reaction to give best phenol conversion. Increasing the amount of solvent to 4 ml and 8 ml, the catalytic reaction always led to the poor performance. A decreased solvent amount (1 ml) was found not sufficient to dissolve the substrate and formed a non-homogeneous reaction mixture.

3.2.1.8. Effect of reaction time. The dependence of the reaction conversion and selectivity on reaction time was studied for 24 h. In general phenol conversion increases with longer reaction times and attains a maximum conversion (39%) within 1.5 h (Fig. 4). The percentage selectivity for formation of catechol and hydroquinone also varies with reaction time. Benzoquinone could not be detected at any stage of the reaction. Selectivity for catechol formation in the product is 100% at the beginning of the reaction. When reaction time is prolonged beyond 3 h, phenol conversion increased slightly, hydroquinone selectivity gradually increased while the catechol selectivity decreased, exhibiting 32.0 and 76.8% at 6 h, respectively. The generation of phenoxy radicals occurs on the catalyst surface which leaves the activated *ortho*-sites lie close to the oxo-complex and would be more amenable to attack by the generated hydroxy radical. This could be the plausible reason that the *ortho*-hydroxylation is the predominant pathway in this catalysis [10c]. After certain reaction time, the catalyst surface could be partially covered by the products which would create partial hindrance for the substrate in approaching the catalyst surface. Thus, there will

Table 6
Catalytic performance in phenol hydroxylation[a], percentage selectivity and turn over frequencies of over the catalysts.

Catalyst	% PhOH conv.	Product distribution (%)			TOF (h^{-1})
		Cat[b]	HQ[c]	Cat/HQ	
[—CH_2{Cu(sal-1,2-pn)}—]$_n$	48.2	67.6	32.4	2.15	142
[—CH_2{Ni(sal-1,2-pn)·2DMF}—]$_n$	40.1	70.7	29.3	2.41	166

[a] Reaction conditions: Phenol (0.05 mol); phenol/H_2O_2 molar ratio = 1; catalyst (10 mg); solvent, CH_3CN (2 ml); reaction time = 6 h; reaction temperature 80 °C.
[b] Cat = Catechol.
[c] HQ = Hydroquinone.

be sufficient time for the OH^- to then attack at the *para*-position. Interestingly, recycled catalysts after regeneration exhibit almost similar catalytic activity and selectivity towards the products. This observation supports the above explanation for the variation of product selectivity with time.

The ratio of formation of catechol to hydroquinone reached to maximum (~2) after 5 h. Both the % conversion and % selectivity were not affected with reaction time after acquiring a steady state. On increasing the reaction time to 24 h, only minor increase in the transformation of phenol as well as percentage selectivity for the formation of catechol and hydroquinone were observed for both types of catalysts.

3.2.1.9. Comparison of catalysts performance. Table 6 and Fig. 4 show the reaction profile for the performance of Cu and Ni-based catalyst for phenol hydroxylation. It is clear that the Cu complex is a better catalyst than the Ni complex as it does not show an induction period and reaction proceeded steadily in a continuous manner. With the former a maximum conversion of ~40% is reached after 1.5 h. When the reaction was prolonged for 6 h, the conversion increased to 48%. The latter gave only 4% conversion after 1.5 h and reached a maximum conversion of 40% after 6 h. The dissimilarities in the induction period for the catalysts can be explained by either slow formation of active peroxo intermediate species or taking a longer time to transfer oxygen to the substrate [1]. Once the active species is generated, this is rapidly converted to products, but acquires a steady state at different times. Both catalysts show effective conversion to catechol (67–71%) with a catechol to hydroquinone ratio of 2:1 (Table 6)

On comparing the catalytic data found herein for the liquid phase hydroxylation of phenol with our data reported earlier on similar Cu(II)- and Ni(II)-salen and salpn coordination polymers, our catalysts show comparable activity with the salen polymeric complexes and lower activity than 1,3-salpn polymeric complexes. This can be attributed to the greater flexibility of the 1,3-salpn ligand compared to the salen and 1,2-salpn ligands and also the branching of the backbone in these catalyst may influence its performance. However, the TOF values for our catalysts are similar or better than that of the above mentioned catalyst analogues (Table 7). Also the results show that Cu(II)- and Ni(II)-polymeric complexes are better catalysts over the corresponding encapsulated ones, the monomeric complexes and TS-1 (Table 7). The neat complexes suffer from dimerization (formation of oxo dimer) which hinders the substrate to reach the active centers of the catalysts [37]. Although the zeolite encapsulated metal complexes do

Table 7
Comparison of Turnover Frequencies (TOF) between our catalysts and related systems for hydroxylation of phenol.

Catalyst	TOF (h^{-1})	Ref.
[—CH_2{Cu(sal-1,2-pn)}—]$_n$	142	This work
[—CH_2{Ni(sal-1,2-pn)·2DMF}—]$_n$	166	This work
[—CH_2{Cu(salen)}—]n	136.7	[24]
[—CH_2{Ni(salen)}—]n	130.3	[24]
[—CH_2{Cu(salpn)}—]n	138.6	[24]
[—CH_2{Ni(salpn)·2DMF}—]n	221.4	[24]
Cu(Salen)-Y	40	9a
Cu(5-Cl-Salen)-Y	88	9a
[Cu(saldien)]-Y	25.0	10e
[Ni(saldien)]-Y	24.6	10e
[Ni(salpn)]-Y	28.7	34b
CuPc-Y	74-8	[35]
Cu(Salen)	21	9a
Cu(5-Cl-Salen)	31	9a
TS-1	5.5	[12]
Meso TS-1	25	[36]

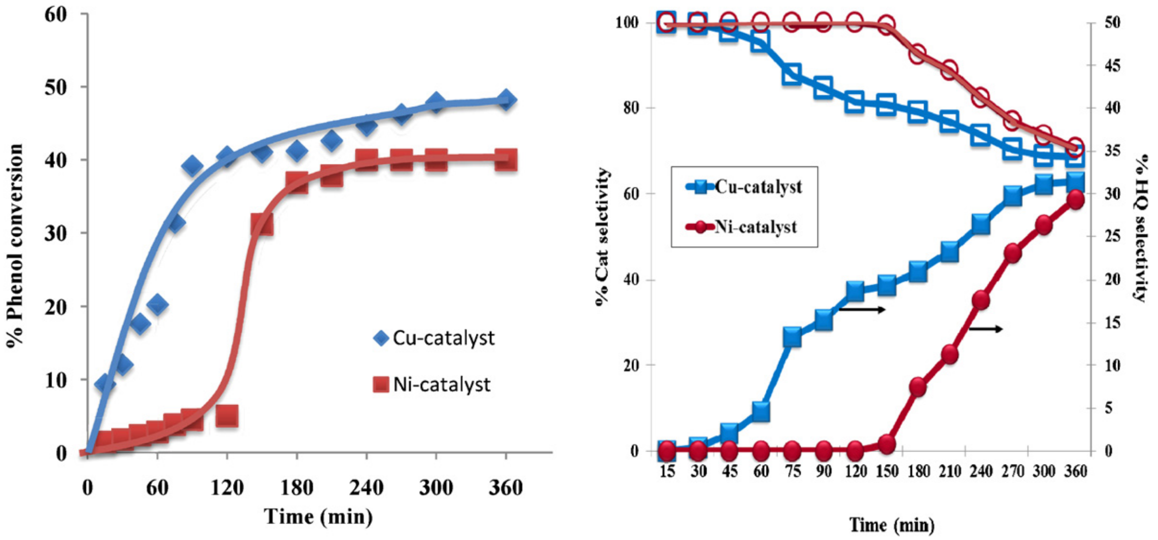


Fig. 4. Catalytic performance in phenol hydroxylation, percentage selectivity and turn over frequencies over the catalysts.

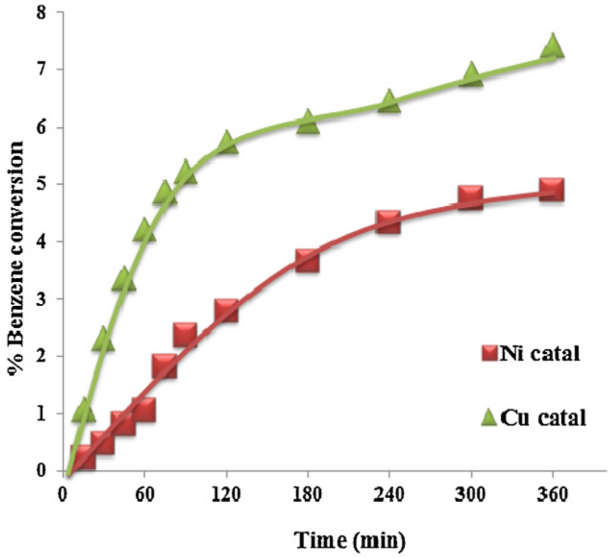


Fig. 5. Kinetic plot for benzene conversion at 70 °C over Ni- and Cu-based catalysts.

not suffer from dimerization, however, fewer metal centres per unit cell of zeolite are available that make their catalytic activity better but still poorer than the polymeric complexes.

The coordination polymers currently being discussed possess many active metal centres available in the chelating polymer pockets this could play a positive role in enhancing the catalytic activity. In addition to the thermal stability and insolubility in common solvents could give them an advantage in heterogeneous catalysis.

3.2.2. Hydroxylation of benzene

Direct liquid phase hydroxylation of benzene using H_2O_2 as an oxidant catalyzed by the synthesized catalysts under the reaction conditions (0.02 mol of benzene, 0.02 mol of H_2O_2 and 0.025 g of catalyst at 70 °C) gave only one product, *i.e.* phenol. Traces of higher oxidation products (<2%) could be detected by using 2:1 (H_2O_2:benzene) molar ratio with partial improvement in % benzene conversion.

To evaluate the efficiency of the two catalysts *viz.*, $[—CH_2\{Cu(sal\text{-}1,2\text{-}pn)\}—]_n$ and $[CH_2\{Ni(sal\text{-}1,2\text{-}pn)\cdot 2DMF\}—]_n$, for the hydroxylation of benzene using 30% H_2O_2 as an oxidant, the percentage of benzene conversion is plotted as a function of time at 70 °C as shown in Fig. 5. The results indicate that conversion of benzene increased with reaction time for both catalysts and attained a steady state after ~3 h. In case of Ni-based catalyst, the benzene conversion was initially low (1.5 h) but improved with time and reached the steady state at ~3 h, thereafter, only a very slow conversion was observed up to 24 h which may be due to inefficient product desorption from the catalyst surface rather than deactivation of the catalyst [38]. The Cu-based catalyst shows better performance (~7%) than Ni-based catalyst (~5%) after 6 h, under the reaction conditions: benzene:H_2O_2 (1:1 molar ratio), catalyst (10 mg); solvent, CH_3CN (2 ml) at 70 °C. The Cu complex does not show an induction period which can be explained that once the active species is generated; it is rapidly converted into products. Both catalysts showed >99% selectivity for producing phenol without any by-product being detected by GC. The selectivity towards phenol formation remained unchanged over a period of 24 h.

Our search of the literature reveals that to date no study has been done on the hydroxylation of benzene using polymeric chelating complexes. Comparing the catalytic activity of our catalysts to other catalytic systems (homogenous and heterogeneous) for the hydroxylation of benzene shows similar or lower activity to these catalysts [6,39–43]. Furthermore the selectivity of our catalysts appears to be highly selective to produce phenol.

3.2.3. Stability and reusability of the catalysts

The stability and reusability of the catalysts were investigated. At the end of the reaction, the catalyst was successfully recovered by first diluting the reaction mixture with acetonitrile followed by filtration. The catalyst was then regenerated by Soxhlet extraction with acetonitrile to remove the organic materials remaining on the catalyst's surface. The catalyst was dried at 120 °C for 6 h. The regenerated catalysts were reused three times under the same reaction conditions. After two successive cycles the activity of the catalysts were found to be comparable with that for the fresh catalysts. Small lowering in the activity (8–10%) occurs after the second cycle.

The experimental observations have indicated that during the reaction there was no metal leaching into the reaction mixture. This is also confirmed by isolating the catalyst from the reaction mixture after 2 h reaction time and the reaction was continued for another 4 h. It was found that the % conversion remained unchanged without any further increase which proved that the reaction is catalyzed heterogeneously. Moreover, the ICP analyses for the reaction filtrate indicates the absence of metal ions which confirm indicate that no leaching has occurred during the reaction.

Comparable IR spectral patterns of fresh and regenerated catalyst indicate that the structure remains unchanged. This suggests that these catalysts could be reused after recovery without significant loss of activity.

4. Conclusion

Coordinated metal complexes of polymeric ligand $[—CH_2(H_2sal\text{-}1,2\text{-}pn)—]_n$ with Cu(II) and Ni(II) metal ions have been synthesized and characterized. The catalytic activity for hydroxylation of phenol using the Cu-based catalyst is higher than the Ni-based catalyst. On the other hand, both catalysts show excellent selectivity towards catechol (67–71%) under the optimum reaction conditions (phenol, 0.05 mol; phenol/H_2O_2 molar ratio = 1; catalyst (10 mg); solvent, CH_3CN (2 ml) reaction temperature 80 °C.

These catalysts were also tested for direct hydroxylation of benzene. Both catalysts show low activity but excellent selectivity towards phenol formation of nearly 100% for the oxidation of benzene under the optimum reaction conditions (0.02 mol benzene, 0.02 mol of H_2O_2 and 0.010 g of catalyst at 70 °C).

The catalysts can be recovered and reused without significant loss of activity. This study would be valuable for developing a new environmentally benign route for oxidation of phenol and benzene.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.05.048.

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