

# Synthesis, characterization and study of polymeric iron(III) complexes with bidentate *p*-hydroxy Schiff bases as heterogeneous catalysts

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## Abstract

The chelating Schiff base ligands 4-(naphthalen-1-yliminomethyl)-phenol (**I**) and 4-(naphthalen-2-yliminomethyl)-phenol (**II**) were obtained by condensation of  $\alpha$ - or  $\beta$ -naphthyl amine respectively, with *p*-hydroxy benzaldehyde. The reaction of the chelating ligands **I** and **II** with iron(III)nitrate in aqueous ethanol afforded new coordination polymer complexes poly-[Fe(C<sub>10</sub>H<sub>7</sub>-1-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] (**III**) and poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] (**IV**). The Schiff bases and their iron(III) complexes were characterized by various physico-chemical techniques. The chemical formulae of compounds were determined by elemental analyses. It was found that both of these ligands acted as bidentate bridging ligands and thus formed cross-linked hexacoordinated polymeric complexes. The coordination was ascertained from the IR, <sup>1</sup>H NMR and UV–Vis Spectral data of the ligand and complexes wherein, a new weak band at 472 and 466 nm were observed due to symmetry forbidden d–d transitions. The azomethine proton signals in the <sup>1</sup>H NMR spectra of the Schiff bases **I** and **II** observed between  $\delta$  8.45 and 8.55 ppm were observed upfield shifted in the spectra of the complexes. The catalytic properties of the coordination polymers as heterogeneous catalysts were examined by liquid phase hydroxylation of phenol using H<sub>2</sub>O<sub>2</sub> as an oxidant. It was found that these complexes provide high TOF value for the hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub>. The % phenol conversion was higher with  $\beta$ -Schiff base complex **IV** but the product distribution was almost the same with either of the complex.

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## 1. Introduction

A wide variety of ligand types are obtained via the Schiff base condensation of primary aromatic amines and aldehydes. These ligands widely vary in their structures, flexibility, electronic nature and the presence of additional donor atoms besides imino nitrogen. Further fine-tuning of their coordination characteristics can be achieved by the variation in the nature and position of the substituents. A large number of transition metal complexes with a variety of acyclic [1–10]

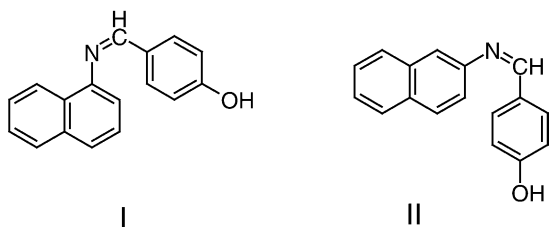
and macrocyclic [11–13] Schiff bases have been prepared and studied extensively. The central metal in these complexes act as active sites and thereby successfully catalyze chemical reactions [14,15].

The Schiff base transition metal complexes are a family of attractive oxidation catalysts for a variety of organic substrates because of their cheap and easy synthesis and their chemical and thermal stability. They are also used to catalyze transformation of simple organic substrates to functionalised derivatives of commercial and synthetic interest [16–19]. The catalytic hydroxylation of phenol to dihydroxy benzenes is one such attractive task. An important challenge in this field is the development of catalysts for selective and efficient conversion of phenol to a particular product. Although, catechol and hydroquinone are the oxidation products of phenol and

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Scheme 1. Structures of the Schiff bases synthesized.

both are commercially important, selective conversion to either product is always desired. They are widely used as photography chemicals, antioxidants and polymerization inhibitors, and also used in pesticides, flavouring agents and medicines.

Schiff bases with linearly disposed multiple donor sites can form coordination polymers in which the metal coordination are exploited to extend the polymeric network structure [20]. The porous structure of the coordination polymers offers potential applications as adsorbents [21,22], catalysts [23] and ion exchangers [24,25], etc. The catalysis using coordination polymers is of current research interest because of the ease of separation of products, recovery of the catalyst, higher stability and above all their reusability after several cycles, which are environmentally benign chemical processes [26]. However, their applications in organic synthesis are limited because of their poorer activity as compared to homogeneous catalysts. As a continuation of research on catalyzed hydroxylation of phenol [27] we report herein (i) synthesis and characterization of two new Schiff bases, viz. 4-(naphthalen-1-yliminomethyl)-phenol (I) and 4-(naphthalen-2-yliminomethyl)-phenol (II) (Scheme 1) and their iron(III) complexes, (ii) investigation of the catalytic activity of these new polymeric complexes for the oxidation of phenol by  $\text{H}_2\text{O}_2$ .

## 2. Experimental

### 2.1. Materials

1- and 2-amino naphthalene, 4-hydroxy benzaldehyde, acetonitrile, *n*-butyl acetate and *n*-heptane were obtained from Aldrich. Absolute ethanol and cyclohexane were obtained from Fluka and the A.R. grade phenol and 30%  $\text{H}_2\text{O}_2$  were obtained from Qualigens. Purified  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was obtained from BDH and was used directly without further purification.

### 2.2. Instrumentations

Melting points were measured on Gallenkamp melting point apparatus, UV–vis spectra on Shimadzu 1601 spectrophotometer and IR spectra on Perkin Elmer 1600 FT-IR as KBr disc.  $^1\text{H}$  NMR spectra were recorded on FT 90 JEOL instrument using TMS as internal reference in DMSO-

$d_6$  solvent. Elemental analyses were carried out on CHN Carlo Erba EA 1108 instrument. Catalytic reaction products were analysed using either Nucon 5700 gas chromatograph equipped with Flame ionization detector, OV-172  $\text{m} \times 2 \text{ mm}$  (i.d.) (S.S.) column and driven by ORACLE2 computer software or on Hewlett Packard HP 5890 equipped with Flame ionization detector and 10  $\text{m} \times 0.53 \text{ mm}$  (i.d.) HP1 capillary column, driven by HP computer software. Cyclic voltammograms were recorded on a CHI-600A electrochemical analyser using a three-electrode assembly in presence of 0.1 M TEAP (in DMF) as supporting electrolytes. Pt wire auxiliary electrode, Ag/AgCl reference electrode and glassy carbon working micro-electrode were used.

### 2.3. Syntheses

#### 2.3.1. Preparation of Schiff bases

The Schiff bases 4-(naphthalen-1-yliminomethyl)-phenol (I) and 4-(naphthalen-2-yliminomethyl)-phenol (II) were prepared by refluxing equimolar amounts of the 4-hydroxybenzaldehyde (2.44 g, 0.02 mol) with 1- or 2-amino naphthalene (2.86 g, 0.02 mol) for 2 h in absolute ethanol (50 mL). Upon cooling, brown crystalline solid separated out that were collected by filtration. They were recrystallized from hot ethanol.

4-(Naphthalen-1-yliminomethyl)-phenol ( $\text{C}_{10}\text{H}_7-1-\text{N}=\text{CH}-\text{C}_6\text{H}_4-4-\text{OH}$ ): Colour yellowish brown. Mp 187–9 °C. Analyses (%): found C, 82.1, H, 5.2, N 5.4; calcd. for  $\text{C}_{17}\text{H}_{13}\text{NO}$  C, 82.5, H, 5.3, N 5.7%.

4-(Naphthalen-2-yliminomethyl)-phenol ( $\text{C}_{10}\text{H}_7-2-\text{N}=\text{CH}-\text{C}_6\text{H}_4-4-\text{OH}$ ): Colour yellowish brown. Mp 226–8 °C. Analyses (%): found C, 82.7, H, 5.1, N, 5.5; calcd. for  $\text{C}_{17}\text{H}_{13}\text{NO}$  C, 82.5, H, 5.3, N 5.7%.

#### 2.3.2. Preparation of iron(III) complexes

A solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.81 g, 2.0 mmol) in 20 mL water was mixed with the solution of corresponding Schiff base I or II (1.73 g, 6.0 mmol) in ethanol (50 mL) and the suspension was stirred for 2 h. The solid product that was formed in either case was collected by filtration. It was successively washed with ethanol, water and then again twice with ethanol. Compounds were dried over  $\text{CaCl}_2$ .

Poly- $[\text{Fe}(\text{C}_{10}\text{H}_7-1-\text{N}=\text{CH}-\text{C}_6\text{H}_4-4-\text{O})_3]$ : Colour dark brown. Mp NM up to 300 °C. Analyses (%): found C, 78.1, H, 5.0, N 5.4, Fe, 7.5; calcd. for  $\text{C}_{51}\text{H}_{36}\text{N}_3\text{O}_3\text{Fe}$  C, 77.1, H, 4.5, N 5.3, Fe, 7.1%. CV (in AN):  $E_p$  0.79, -0.91, -1.25 V versus Ag/AgCl.

Poly- $[\text{Fe}(\text{C}_{10}\text{H}_7-2-\text{N}=\text{CH}-\text{C}_6\text{H}_4-4-\text{O})_3]$ : Colour dark brown. Mp NM up to 300 °C. Analyses (%): found C, 77.9, H, 5.1, N 5.8, Fe, 7.7; calcd. for  $\text{C}_{51}\text{H}_{36}\text{N}_3\text{O}_3\text{Fe}$  C, 77.1, H, 4.5, N 5.3, Fe, 7.1%. CV (in AN):  $E_p$  0.83, -0.85, -1.10 V versus Ag/AgCl.

#### 2.3.3. Catalytic reaction

The catalytic experiments were carried out in a 50 mL two-necked round bottomed flask fitted with a water condenser

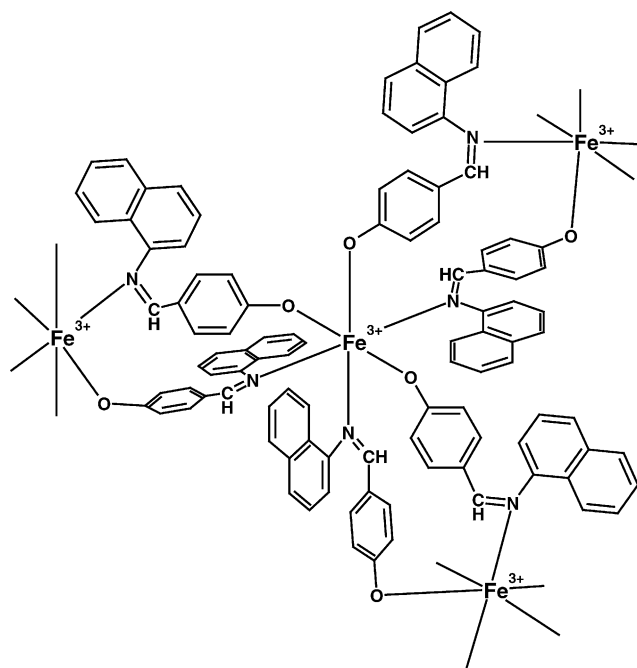
and kept in an oil bath with continuous stirring. In a typical hydroxylation reaction, the solid catalyst (4 mg) was added to a mixture of the substrate (phenol) 4.7 and 5.67 g 30% H<sub>2</sub>O<sub>2</sub> in 2 mL MeCN at 80 °C. Addition of the catalyst was considered the starting point of the reaction. The progress of the oxidation was monitored through periodic withdrawal of small amount of aliquots and analysing them by gas chromatograph.

### 3. Results and discussion

The Schiff bases 4-(naphthalen-1-yliminomethyl)-phenol (**I**) and 4-(naphthalen-2-yliminomethyl)-phenol (**II**), are highly soluble in polar organic solvents but are only moderately soluble in alcohol. They conveniently formed complexes with the iron(III) metal ion. Unlike the uncomplexed ligands, their iron(III) complexes are insoluble in water and are only sparingly soluble in alcohol and in less polar organic solvents. Instead, they exhibit moderate solubility in DMF and DMSO. Considering the nature of the ligands, and solubility behaviours of the complexes they seem to consist of three-dimensional polymeric structures as shown below. The chemical compositions of the ligands and the coordinated metal complexes were confirmed from their elemental analyses and IR, electronic and <sup>1</sup>H NMR spectral data. It was found that coordination complexes possess metal/Schiff base in 1:3 molar ratio. They might possess random combination of *mer*-FeO<sub>3</sub>N<sub>3</sub> and *fac*-FeO<sub>3</sub>N<sub>3</sub> coordination environments (Scheme 2).

#### 3.1. Electronic spectra

The electronic spectra of the ligands 4-(naphthalen-1-yliminomethyl)-phenol (**I**) and 4-(naphthalen-2-yliminomethyl)-phenol (**II**) were recorded in absolute ethanol and cyclohexane while, those of the iron(III) complexes in DMF. The electronic absorption bands are listed in Table 1.



Scheme 2. Suggested structure of the polymeric iron(III) complex with 4-(naphthalen-1-yliminomethyl)-phenol Schiff base.

The  $\alpha$ -naphthyl amine Schiff base ligand 4-(naphthalen-1-yliminomethyl)-phenol (**I**) exhibited bands at 207, 229, 284, 300 and 340 nm and that of  $\beta$ -naphthyl amine Schiff base ligand 4-(naphthalen-2-yliminomethyl)-phenol (**II**) exhibited bands at 214, 226, 278, 287 and 332 nm. These bands could be assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The strong bands in the UV region are characteristic of Schiff bases, e.g. in benzilidianeiline two absorption bands are observed. The first band which appears at 262 nm is assigned to  $\pi \rightarrow \pi^*$  transition. The second band which appears at 312 nm is attributed to  $n \rightarrow \pi^*$  transition [4]. The ligand centered electronic absorption bands undergo only moderate shifting upon metal coordination. Hence the complexes show almost all bands at nearly the same position with only slight shift in the positions of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  bands.

Table 1  
Electronic absorption spectral data with assignment of Schiff bases and their iron(III) complexes at 25 °C

Compound	$\lambda_{\max}$ ( $\epsilon$ , $\text{m}^2 \text{mol}^{-1}$ ) in ethanol		$\lambda_{\max}$ in cyclohexane
C <sub>10</sub> H <sub>7</sub> -1-N=CH-C <sub>6</sub> H <sub>4</sub> -4-OH	340 (1058)	$n \rightarrow \pi^*$	343
	300 (1575)		290
	284 (1383)sh	$\pi \rightarrow \pi^*$	272
	229 (3625)		230
	207 (4110)		211
Poly-[Fe(C <sub>10</sub> H <sub>7</sub> -1-N=CH-C <sub>6</sub> H <sub>4</sub> -4-O) <sub>3</sub> ]	472 (180)		
C <sub>10</sub> H <sub>7</sub> -2-N=CH-C <sub>6</sub> H <sub>4</sub> -4-OH	332 (2050)	$n \rightarrow \pi^*$	328
	287 (2575)		282sh
	278 (2400)sh	$\pi \rightarrow \pi^*$	274
	226 (4200)		227
	214 (3000)sh		210sh
Poly-[Fe(C <sub>10</sub> H <sub>7</sub> -2-N=CH-C <sub>6</sub> H <sub>4</sub> -4-O) <sub>3</sub> ]	466 (150)		

sh = shoulder.

Table 2  
<sup>1</sup>H NMR data for Schiff base ligands and their iron(III) complexes

Compound	δ (ppm)		
	–N=CH	Ar–H	Phenolic–H
C <sub>10</sub> H <sub>7</sub> –1-N=CH–C <sub>6</sub> H <sub>4</sub> –4-OH	8.45 (s, 1H)	6.90–8.2 (m, 11H)	12.88 (s, 1H)
Poly-[Fe(C <sub>10</sub> H <sub>7</sub> –1-N=CH–C <sub>6</sub> H <sub>4</sub> –4-O) <sub>3</sub> ]	1.30 (s, 1H)	6.85–8.3 (m, 11H)	–
C <sub>10</sub> H <sub>7</sub> –2-N=CH–C <sub>6</sub> H <sub>4</sub> –4-OH	8.55 (s, 1H)	6.95–8.3 (m, 11H)	12.95 (s, 1H)
Poly-[Fe(C <sub>10</sub> H <sub>7</sub> –2-N=CH–C <sub>6</sub> H <sub>4</sub> –4-O) <sub>3</sub> ]	1.45 (s, 1H)	6.90–8.3 (m, 11H)	–

The electronic spectra of these polymeric complexes were also taken in ethanol. In the electronic spectrum of poly-[Fe(C<sub>10</sub>H<sub>7</sub>–1-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] and poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] complexes i.e. with α- and β-Schiff bases, a new weak band were observed at 472 and 466 nm, respectively, along with other ligand centered strong bands. These new absorption bands could be assigned to symmetry forbidden weak d–d transitions.

From Table 1 it can be concluded that the polarity of the solvent affected the CT absorption band. When the spectra were taken in non-polar solvent (cyclohexane) a red shift has taken place and this indicate that the excited state of the Schiff bases is more polar than its ground state.

### 3.2. <sup>1</sup>H NMR

The <sup>1</sup>H NMR spectra of both ligands, i.e. 4-(naphthalen-1-yliminomethyl)-phenol (**I**) and 4-(naphthalen-2-yliminomethyl)-phenol (**II**) are almost similar. Both of them showed a very downfield singlet signal at δ 12.88 and 12.95 ppm, respectively. The aromatic protons are observed as complex multiplets between δ 6.9 and 8.3 ppm (Table 2). The azomethine proton signals are observed as singlets in the region δ 8.45 and 8.55 ppm, respectively, that are consistent with the previous work on other Schiff bases [3]. The NMR spectra of the complexes show that the azomethine proton signals are shifted upfield to δ 1.3 ppm upon complexation in α-Schiff base complex poly-[Fe(C<sub>10</sub>H<sub>7</sub>–1-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] and to δ 1.45 ppm in β-Schiff base complex poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>]. The phenolic proton signals are not observed in the complexes which suggests that they bind with the metal ion as monoanion.

### 3.3. IR spectra

IR spectra of both Schiff bases show a strong sharp band in the region 1600–1610 cm<sup>–1</sup> which are characteristics of C=N stretching vibration in addition to a broad band due to the hydrogen bonded hydroxyl stretching vibration, in the region ~3300 cm<sup>–1</sup>. Upon complexation with the iron(III) in poly-[Fe(C<sub>10</sub>H<sub>7</sub>–1-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>], poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] complexes the C=N stretching band shift to higher frequency. Also there appeared two or three new bands in the region between 420 and 540 cm<sup>–1</sup>, that could be attributed to Fe–N and Fe–O stretch-

ing vibrations. They were observed as weak bands [28]. These new bands in the IR spectra of the coordination polymers are indicative of the formation of the iron(III) complexes.

Several absorption bands were observed between 2700 and 3200 cm<sup>–1</sup>, which appeared at the same position for both ligands and metal chelates, can be assigned to C–H stretching vibrations of azomethine CH and aromatic CH vibrations. The phenolic OH stretching band in the region ~3300 cm<sup>–1</sup> disappeared upon complexation with the iron(III), which further indicated the coordination of the Schiff bases in the deprotonated form.

### 3.4. Catalytic activity studies

Catalytic role of the polymer complexes poly-[Fe(C<sub>10</sub>H<sub>7</sub>–1-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] and poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] for the hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub> were investigated in acetonitrile. Since they are only sparingly soluble in acetonitrile the catalyzed reactions are primarily heterogeneous. Hydroxylation reactions were carried out employing different amounts of phenol and H<sub>2</sub>O<sub>2</sub> in acetonitrile at 80 °C and other temperatures. Two products, catechol and hydroquinone, are usually formed in the catalytic hydroxylation of phenol. However, in certain cases, a second oxidation of hydroquinone occurs leading to formation of *p*-benzoquinone [29]. In our studies *p*-benzoquinone was detected especially when high concentration of H<sub>2</sub>O<sub>2</sub> was used but in other cases *p*-benzoquinone was not detected. The *meta*-dihydroxy benzene (i.e. resorcinol) was not formed in any case. Two different catalysts, viz. poly-[Fe(C<sub>10</sub>H<sub>7</sub>–1-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] and poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] were used. Due to better performance and steric considerations at Fe<sup>3+</sup> centre the β-imine complex poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] was chosen as a representative catalyst to optimize the reaction conditions. Various modifications in the reaction conditions aimed to achieve higher catalytic conversion efficiency.

#### 3.4.1. Influence of reaction temperature

In order to study the effect of temperature on the catalyst performance, reactions were investigated for the chosen catalyst poly-[Fe(C<sub>10</sub>H<sub>7</sub>–2-N=CH–C<sub>6</sub>H<sub>4</sub>–4-O)<sub>3</sub>] at three different temperatures 50, 65 and 80 °C. Other parameters, viz. amount of phenol (0.05 mol), H<sub>2</sub>O<sub>2</sub> (0.05 mol), catalyst (0.004 g) and solvent CH<sub>3</sub>CN (2 mL) were kept fixed. Fig. 1

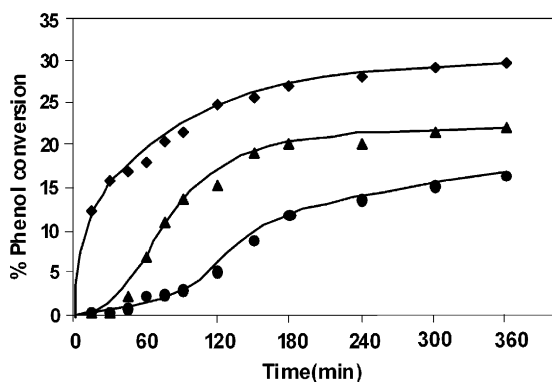


Fig. 1. Effect of reaction temperature on the % phenol conversion as a function of time in presence of poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] complex as catalyst: (●) 50 °C, (▲) 65 °C, (◆) 80 °C.

shows the relationship between the percentage phenol conversion and the reaction time at three different reaction temperatures. This shows that the reaction rate was lower at low temperature of 50 °C. At 80 °C in refluxing acetonitrile, reaction gives the maximum percentage conversion of phenol (29.6%). This also has an added advantage of early completion >90% conversion of phenol in a shorter duration of around 3 h. Whereas, the percentage conversion at 50 and 65 °C are lower i.e. 16.4% and 22%, respectively, and need higher duration to reach the maximum percentage conversion. The reaction at 80 °C is much faster than at 65 and 50 °C. The product selectivity along with catechol to hydroquinone in molar ratios and TOF values are presented in Table 3.

#### 3.4.2. Influence of H<sub>2</sub>O<sub>2</sub> concentration

The influence of H<sub>2</sub>O<sub>2</sub>:phenol ratio on phenol hydroxylation is presented in Fig. 2. Three different H<sub>2</sub>O<sub>2</sub>:phenol molar ratio (0.5:1, 1:1 and 2:1) were used in this study. It is clearly shown that 2:1 gave the maximum percentage conversion (41.1%). On the other hand the 1:1 molar ratio of the oxidant/substrate gave 29.6% over all phenol conversion. The % H<sub>2</sub>O<sub>2</sub> efficiency was much higher (31%) with 1:1 molar ratio of H<sub>2</sub>O<sub>2</sub>:phenol whereas, it was 20% in case of 2:1 ratio. Using 0.5:1 molar ratio i.e. H<sub>2</sub>O<sub>2</sub> in half molar amount of phenol, the over all percentage conversion was much lower (20%) but had a 38% H<sub>2</sub>O<sub>2</sub> efficiency (Table 4). Therefore, the 1:1 molar ratio was taken as the best ratio to get maxi-

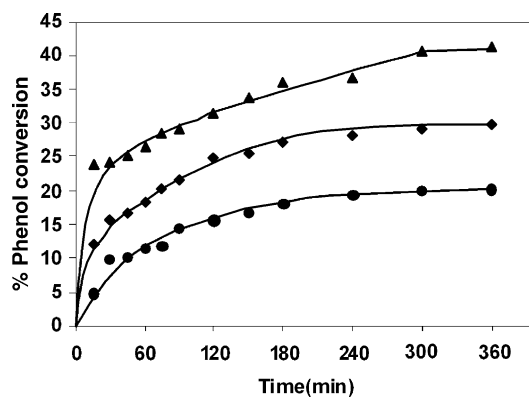


Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub>:phenol molar ratio (▲) 2:1, (◆) 1:1, (●) 0.5:1 on % phenol conversion as a function of time in presence of catalyst poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>].

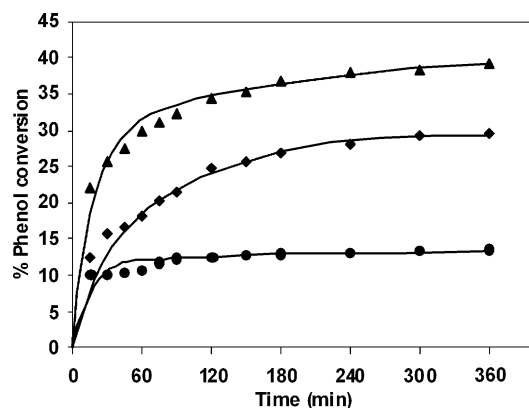


Fig. 3. Effect of phenol concentration on hydroxylation reaction of phenol as a function of time catalyzed by poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] complex in presence of 0.05 mol H<sub>2</sub>O<sub>2</sub>:phenol (▲) 0.025 mol, (◆) 0.05 mol, (●) 0.1 mol.

imum percentage conversion and maximum H<sub>2</sub>O<sub>2</sub> efficiency as well as high TOF value of 486 (Table 4).

#### 3.4.3. Influence of phenol concentration

To investigate the influence of moles of phenol (substrate) on the hydroxylation of phenol, three different weights of phenol were used 2.35, 4.7 and 9.4 g (0.025, 0.05 and 0.10 mol, respectively), while keeping all the other parameters fixed (5 mL H<sub>2</sub>O<sub>2</sub>, 0.004 g catalyst in 2 mL MeCN at 80 °C). It is clear from Fig. 3 that with 1:1 H<sub>2</sub>O<sub>2</sub>:PhOH molar ratio (i.e. 4.7 g PhOH) a maximum of 29.6% overall conversion was obtained. When phenol was taken in half molar amount to that of H<sub>2</sub>O<sub>2</sub>, 1:0.5 molar ratio a maximum of 39.1% conversion was obtained. Increasing the amount of PhOH to twice of H<sub>2</sub>O<sub>2</sub>, the overall conversion was lowered to 13.5%. However, comparing % H<sub>2</sub>O<sub>2</sub> efficiency for these ratios it is found that 1:1 molar ratio is the best ratio to obtain maximum % conversion with reasonable percentage H<sub>2</sub>O<sub>2</sub> efficiency and also high TOF value. This is in the agreement with the effect of H<sub>2</sub>O<sub>2</sub> concentration.

Table 3

Effect of reaction temperature on % phenol conversion<sup>a</sup>, product selectivity and TOF values

Reaction temperature (°C)	Phenol conversion (%)	Product selectivity (%)		CAT/HQ ratio	TOF (h <sup>-1</sup> )
		Catechol	Hydroquinone		
50	16.4	85.3	14.7	5.8	270
65	22.0	76.6	23.4	3.3	360
80	29.6	70.2	29.8	2.4	486

TOF (h<sup>-1</sup>): turn over frequency = moles of substrate converted per mole of the catalyst per hour.

<sup>a</sup> Reaction conditions: phenol (0.05 mol); phenol/H<sub>2</sub>O<sub>2</sub> molar ratio = 1; catalyst = 4 mg; solvent, CH<sub>3</sub>CN (2 mL); reaction time = 6 h.

Table 4  
Effect of H<sub>2</sub>O<sub>2</sub>:PhOH molar ratio on the percent phenol conversion<sup>a</sup>, product selectivity and percent H<sub>2</sub>O<sub>2</sub> efficiency

Molar ratio (H <sub>2</sub> O <sub>2</sub> :PhOH)	Phenol conversion (%)	H <sub>2</sub> O <sub>2</sub> efficiency (%) <sup>b</sup>	Catechol formation (%)	Hydroquinone formation (%)	TOF (h <sup>-1</sup> )
0.5:1	20.0	38	80.8	19.2	330
1:1	29.6	31	78.2	21.8	486
2: 1	41.1	20	74.5	25.5	676

<sup>a</sup> Reaction conditions: phenol (0.05 mol); catalyst = 4 mg; solvent, CH<sub>3</sub>CN (2 mL); reaction time = 6 h; reaction temperature 80 °C.

<sup>b</sup> % H<sub>2</sub>O<sub>2</sub> efficiency = (moles of H<sub>2</sub>O<sub>2</sub> utilized in products formation/moles of H<sub>2</sub>O<sub>2</sub> added) × 100.

#### 3.4.4. Influence of type of solvent

The catalytic activity for hydroxylation of phenol using poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] catalyst seems to be sensitive to the nature of solvent used in the reaction mixture (Fig. 4). There are many factors, which can influence the reaction rates e.g. polarity, differential solvation power, donor ability, electrophilic behaviour and the size of the solvent molecule. It is clear from the figure that acetonitrile is the best solvent in comparison to *n*-butyl acetate and *n*-heptane. Although it is difficult to explain the effect of solvent and to identify the solvent parameters that are responsible for controlling the reaction rate, yet it is clear that the type of solvent has a very significant role in controlling the overall % conversion of phenol. In terms of catechol to hydroquinone formation it was found that the solvent has a moderate influence. It was found that *n*-butyl acetate was more selective to catechol formation (85.5) than the other two solvents. The catechol formation was found to be 85.5% and 77.6% with *n*-butyl acetate and *n*-heptane respectively, while in presence of acetonitrile 70.2% catechol was formed.

#### 3.4.5. Influence of amount of catalyst

The effect of catalyst amount on the rate of reaction is illustrated in Fig. 5. Three different amounts of catalyst, viz. 2, 4 and 8 mg were taken for the fixed amount of phenol (4.7 g) and 30% H<sub>2</sub>O<sub>2</sub> (5 mL) in 2 mL of MeCN at 80 °C. It was observed that on increasing the amount of catalyst from 2 to

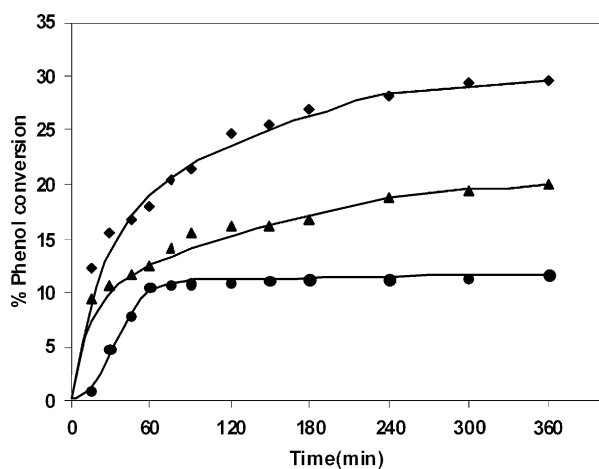


Fig. 4. Effect of type of solvent on the hydroxylation of phenol catalyzed by poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] complex: 2 mL (♦) CH<sub>3</sub>CN, (▲) *n*-heptane, (●) *n*-butyl acetate.

4 mg, the rate of oxidation and overall conversion of phenol both increased from 18.6% to 29.6% with more than 90% of total conversion achieved in initial 3 h. Further increase in the amount of catalyst (8 mg) only marginally increased the overall conversion (30.7% conversion). This may be due to fast decomposition of H<sub>2</sub>O<sub>2</sub> in presence of excess of the catalyst. Hence, it could be concluded that the reaction is of catalytic nature and 4 mg of the catalyst is sufficient to get the higher phenol conversion. From Table 5 it could be concluded that the best molar ratio of phenol to the catalyst used is 9923. This has been supported by the high value of TOF at 4 mg weight of the catalyst. Hence taking higher amount of the catalyst is not economical.

#### 3.4.6. Influence of the oxidant

Various types of oxidants can be employed in the oxidation reactions. Hydrogen peroxide is a preferred oxidant as it is environment friendly and produces only water as a by-product. It is a strong oxidizing agent and shows good selectivity for many oxidations [30]. The reactions were carried out using oxidants other than H<sub>2</sub>O<sub>2</sub>, namely 70% aqueous *tert*-butylhydroperoxide (TBHP) and sodium hypochlorite solution, NaOCl (available chlorine ≥4%) (Fig. 6). None of these oxidants were able to hydroxylate phenol to a significant extent under similar reaction conditions. The overall conversion obtained were less than 4%. It seems that these oxidants failed to generate active oxidant species and also had solubility problems associated with the reactant vis-à-vis the oxidant which is in agreement to our results [31].

#### 3.4.7. Effect of time

The catalytic hydroxylation of phenol, using H<sub>2</sub>O<sub>2</sub> as oxidant was studied as a function of time and the results on the

Table 5  
Effect of catalyst weight on phenol hydroxylation

Catalyst weight (g)	Phenol/catalyst molar ratio	Overall % phenol conversion <sup>a</sup>	TOF (h <sup>-1</sup> )
0.002	19845	18.6	615
0.004	9923	29.6	491
0.008	4961	30.7	254

Reaction conditions: phenol (0.05 mol); phenol/H<sub>2</sub>O<sub>2</sub> molar ratio = 1; solvent, CH<sub>3</sub>CN (2 mL); reaction temperature 80 °C. TOF (h<sup>-1</sup>): turn over frequency = moles of substrate converted per mole of metal (in solid catalyst) per hour.

<sup>a</sup> Reaction time 6 h.

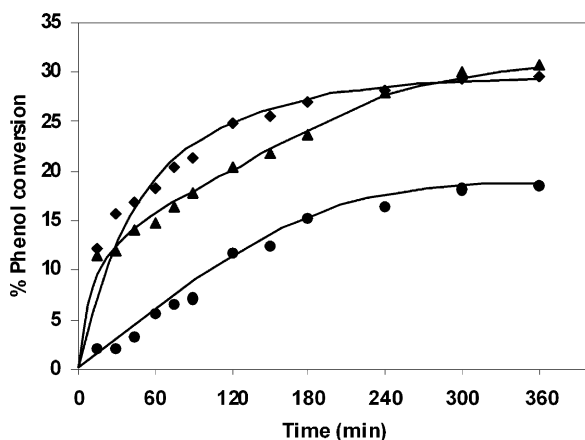


Fig. 5. Effect of amount of catalyst, poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] on phenol hydroxylation: (●) 2 mg, (◆) 4 mg, (▲) 8 mg.

percentage phenol conversion as well as the product selectivity with time are summarized in Table 6. It shows that the percentage conversion of phenol increased with time until a steady state occurs after a certain time, whereas the selectivity towards catechol decreased with increasing reaction time. Both the % conversion and % selectivity were not affected with reaction time after acquiring a steady state.

#### 3.4.8. Comparison between the catalysts

A comparison of the effect of  $\alpha$ - and  $\beta$ -naphylimine complexes i.e. poly-[Fe(C<sub>10</sub>H<sub>7</sub>-1-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>], poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>], on the catalyzed hydroxylation were made. Results are shown in Fig. 7. It is seen that the  $\beta$ -naphylimine complex is a better catalyst than the  $\alpha$ -naphylimine complex. With the former a maximum conversion of 26% after a period of 2 h was obtained and a maximum conversion of 31% obtained after 6 h. The latter gave only 13% conversion in the first hour and

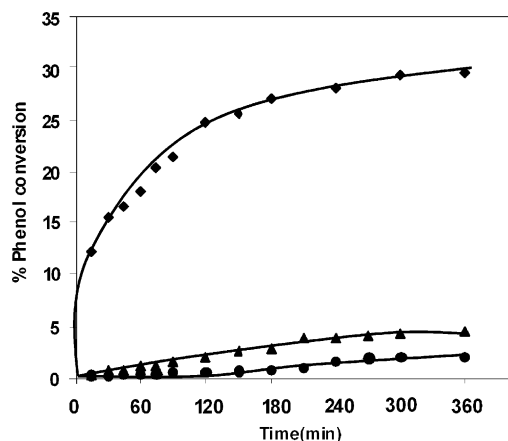


Fig. 6. Effect of oxidant on the hydroxylation of phenol as a function of time in presence of poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] complex as catalyst: (◆) H<sub>2</sub>O<sub>2</sub>, (●) NaOCl, (▲) TBHP.

Table 6

Effect of reaction time on % phenol conversion and product selectivity

Reaction time (min)	Phenol conversion (%)	Product selectivity (%)	
		Catechol	Hydroquinone
15	12.2	88.4	11.6
30	15.6	86.6	13.4
45	16.7	86.8	13.2
60	18.1	86.1	13.9
75	20.3	85.9	14.1
90	21.4	85.2	14.8
120	24.8	83.5	16.5
150	25.6	82.1	17.9
180	27.0	81.3	18.7
240	28.1	80.4	19.6
300	29.3	79.9	20.1
360	29.6	78.2	21.8
1440	30.7	75.7	24.3

Reaction conditions: phenol (0.05 mol); phenol/H<sub>2</sub>O<sub>2</sub> molar ratio = 1; catalyst 20 mg; solvent CH<sub>3</sub>CN (2 mL); reaction time = 6 h; at 80 °C.

reached to the steady state (18.6%) after 6 h. The percentage phenol conversion, selectivity towards the products along with the TOF value after 6 h reaction time is presented in Table 7.

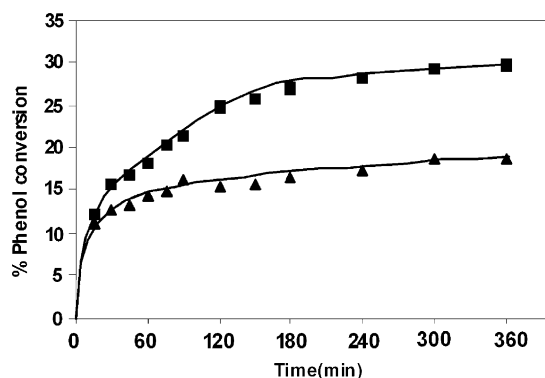


Fig. 7. Kinetic plot for phenol conversion at 80 °C over: (■) poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>], (▲) poly-[Fe(C<sub>10</sub>H<sub>7</sub>-1-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>].

Table 7  
Effect of the nature of the catalyst of phenol oxidation by H<sub>2</sub>O<sub>2</sub>

Catalyst	Phenol conversion (%)	Product selectivity (%)		TOF (h <sup>-1</sup> )
		Catechol	Hydroquinone	
Poly-[Fe(C <sub>10</sub> H <sub>7</sub> -1-N=CH-C <sub>6</sub> H <sub>4</sub> -4-O) <sub>3</sub> ]	29.6	78.2	21.8	491
Poly-[Fe(C <sub>10</sub> H <sub>7</sub> -2-N=CH-C <sub>6</sub> H <sub>4</sub> -4-O) <sub>3</sub> ]	18.6	85.5	14.5	308

#### 4. Conclusion and mechanism

The Schiff base complexes were characterized as coordination polymer, poly-[Fe(C<sub>10</sub>H<sub>7</sub>-1-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] and poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>]. They efficiently catalyzed oxidation of phenol by H<sub>2</sub>O<sub>2</sub>. The catalytic oxidation of phenol gave a mixture of two products, viz. catechol and hydroquinone, due to *ortho* and *para* directing nature of the hydroxyl group. Both of these catalysts exhibited a very high degree of selectivity and catechol was obtained as the major product. The further oxidation of the hydroquinone to benzoquinone was not observed. Owing to the limited solubility of poly-[Fe(C<sub>10</sub>H<sub>7</sub>-1-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] and poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] in acetonitrile water mixture it is likely that they could act as heterogeneous catalysts. However, as the catalytic efficiency was remarkably high in presence of coordinating solvent i.e. acetonitrile vis-à-vis other less coordinating solvents, it is equally likely that reaction proceeded through the dissolved part of the complexes. In the a good coordinating solvent like acetonitrile, the polymeric network is likely to undergo solvent assisted breakdown forming solvated fragments. These solvated species could act as active sites for the catalyzed oxidation of the phenol. The reaction could also proceed at the surface of the undissolved particles where due to partial ligand dissociation solvated (vacant) sites are created. Either of these pathways is assisted in the good coordinating solvents.

Although, formation of Fe(IV)=O species are also suggested in many other catalytic oxidations processes [32]. But, the electrochemical oxidation of poly-[Fe(C<sub>10</sub>H<sub>7</sub>-1-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] and poly-[Fe(C<sub>10</sub>H<sub>7</sub>-2-N=CH-C<sub>6</sub>H<sub>4</sub>-4-O)<sub>3</sub>] complexes using cyclic voltammetry technique, it was found that these complexes exhibit irreversible oxidation waves at much positive potentials (~0.80 V versus Ag/AgCl) in acetonitrile, which is not achievable by H<sub>2</sub>O<sub>2</sub> oxidation. Therefore it is likely that the H<sub>2</sub>O<sub>2</sub> formed hydroperoxo complexes with solvated iron centers and these hydroperoxo complexes undergo further reaction with the phenol.

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