



# Catalytic and electrocatalytic wet oxidation of phenol using two new nickel(II) tetraazamacrocycle complexes under heterogeneous conditions

Vipin Kumar Bansal<sup>a</sup>, Pompozhi Protasis Thankachan<sup>a,\*</sup>, Rajendra Prasad<sup>b</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology Roorkee, IIT Campus, Roorkee, Uttarakhand 247667, India

<sup>b</sup> School of Chemical Sciences, Faculty of Science and Technology, The University of the South Pacific, Suva, Fiji

## ARTICLE INFO

### Article history:

Received 1 July 2009

Received in revised form 3 October 2009

Accepted 8 October 2009

Available online 27 November 2009

### Keywords:

Phenol

Heterogeneous catalysis

Nickel (II) macrocycle

Wet oxidation

## ABSTRACT

Two new tetraazamacrocycle complexes, namely, 7,16-dinicotinoyl[Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}] and 7,16-diisonicotinoyl[Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}] (where [Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}] = 5,7,12,14-tetramethyldi-4-methylbenzo[*b*,*i*][1,4,8,11]tetraazacyclo-tetradecahexaenatonickel(II)) were synthesized by acylation of [Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}] and characterized using spectral and microanalytical data. All tetraazamacrocycle complexes were found to catalyze chemical oxidation of phenol by H<sub>2</sub>O<sub>2</sub> to catechol and hydroquinone and it is found that 7,16-diisonicotinoyl[Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}] showed the best performance. Catechol as the major product and hydroquinone as the minor were characterized respectively under optimal values of some parameters such as amount of catalyst, reaction temperature, oxidant and substrate concentration, effect of reaction media and reaction time. Electrocatalytic oxidation of phenol on glassy carbon electrode modified by the synthesized macrocycle complexes has also been studied.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Transition metal complexes are successfully used as homogeneous and heterogeneous catalysts in various chemical reactions such as epoxidation of olefins [1,2], oxidation of alcohols [3–5], thioethers [6], cyclohexane [7,8], cyclohexene [8], styrene [6,8] and oxyfunctionalization of hydrocarbon to produce valuable aldehydes, ketones, alcohols, etc. [9–12], as intermediate chemicals for the manufacture of commercial products in common use. Heterogeneous catalysis is often more convenient than homogeneous catalysis because recyclability and insolubility in the reaction medium makes the separation of the product and unreacted reactant easy.

Phenol is commonly used as raw material in many chemical, petrochemical, pharmaceutical, textile and agricultural industries. Catalyzed wet oxidation of phenol is at present widely investigated with the dual objectives of removal of phenolic wastes in surface water streams and industrial effluents and of achieving regioselective oxidation to get specific products. In fixed bed reactors where high temperature and pressure are employed, oxidation of phenol gives CO<sub>2</sub>, formic acid, acetic acid maleic acid and oxalic acid as the final products [13]. However, under mild conditions catalytic oxidation of phenol gives catechol and hydroquinone (Scheme 1)

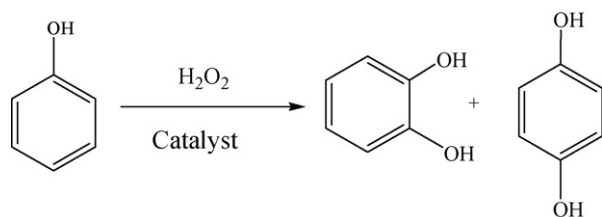
[3,4] and in some cases para benzoquinone has also been observed. Catechol and its derivatives are widely used as flavouring agents, perfumes, antioxidants, photographic developers, and in the pesticide, and pharmaceutical industries. The catalyzed hydroxylation of phenols could be carried out using hydrogen peroxide [3,4], alkyl hydro peroxides, cerium ammonium nitrate [14], mineral acids [15], lead tetraacetate [16], Fermy's salt [17] and other oxidants. Although organic peroxides are stronger oxidizing agents than hydrogen peroxide, the use of hydrogen peroxide as oxidant is preferable due to its excellent green oxygen donor ability. Secondly it generates only water as a by-product, whereas organic peroxides and other oxidants produce hazardous residues. Moreover, hydrogen peroxide also shows good selectivity for *o*, *p*-hydroxylation of phenol.

Several workers have carried out oxidation of phenol using various types of square-planar metallo-complexes as homogeneous [3,4] and heterogeneous catalyst in pure form or immobilized on solid supports like alumina [18], silica [19], zeolites [20–22], polymers [23], carbon nanotube [24,25], etc. Nickel(II) salicylaldimine, amine, imidazole and tetraazamacrocycle complexes have been successfully employed as catalysts in the oxidation of phenol to catechol and hydroquinone [4,19–21].

In this paper we report the synthesis and spectral characterization of two new nickel(II) macrocycle complexes 7,16-dinicotinoyl[Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}], (Ni-Nic) and 7,16-diisonicotinoyl [Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}], (Ni-Iso) (where [Ni{Me<sub>4</sub>(4-MeBzo)<sub>2</sub>[14]tetraaeneN<sub>4</sub>}] = 5,7,12,14-tetramethyldi-4-

\* Corresponding author. Tel.: +91 1332 285331; fax: +91 1332 273560.

E-mail address: [ppthnfcy@iitr.ernet.in](mailto:ppthnfcy@iitr.ernet.in) (P.P. Thankachan).



**Scheme 1.** Catalytic oxidation of phenol in presence of  $\text{H}_2\text{O}_2$ .

methylbenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II)). Their characteristics as chemical and electrochemical catalysts have also been studied. The catalytic activity of these complexes as heterogeneous catalyst towards wet chemical oxidation of phenol using  $\text{H}_2\text{O}_2$  as oxidant has been investigated. The reaction conditions were optimized, in term of temperature, effect of reaction media, amount of catalyst, reaction time and relative amounts of oxidant and phenol. Electrocatalytic oxidation of phenol at glassy carbon electrode modified by the synthesized macrocycle complexes has also been investigated.

## 2. Experimental

### 2.1. Materials and methods

Phenol, nickel acetate tetrahydrate and 30%  $\text{H}_2\text{O}_2$  (Rankem, India), nicotinic acid (Loba Chemie, India), 3, 4-diaminotoluene (Sigma Aldrich, USA) and isonicotinic acid (Acros Organics, USA) were used in this study. Acetylacetone, thionyl chloride and triethylamine were obtained from Loba Chemie (India). Tetraethylammonium perchlorate (TEAP) used in cyclic voltammetry studies was obtained from Fluka (Switzerland). All solvents were of analytical reagent grade purchased from Rankem (India). Solvents were purified before their use in the electrochemical studies and synthesis. The acetonitrile used in the electrochemical studies was dried over  $\text{P}_2\text{O}_5$  and distilled while benzene used for the synthesis of acid chloride and for electrochemical studies was dried over sodium wire and distilled.

### 2.2. Instrumentation

Electronic spectra of all macrocycle complexes were recorded on a Shimadzu UV-1601 spectrophotometer in  $\text{CHCl}_3$ ,  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX-500 spectrometer in chloroform-*d*. IR spectra were taken on a Thermo Nicolet Nexus aligent 1100 FT-IR in KBr. The FAB mass spectra tetraazamacrocycle complexes were recorded on Jeol SX-102/DA-6000 mass spectrometer in 3-nitrobenzyl alcohol matrix using xenon as FAB gas. Elemental analyses were carried out on an Elementar Vario EL III analyzer. Electrochemical studies were carried out on a CHI 600A electrochemical analyzer. Three-electrode assembly with Ag/AgCl/KCl (sat.) as reference electrode, Pt wire as counter electrode and glassy carbon as working electrode were used. All electrochemical investigations were carried out in dry benzene/acetonitrile (1:1, v/v) mixture in presence of tetraethylammonium perchlorate (TEAP) as supporting electrolyte while oxidation of phenol on modified electrode was carried out in doubly distilled water using phosphate buffer (0.1 M, pH 7.3) as supporting electrolyte. Catalyzed chemical oxidations were carried out in a flask immersed in controlled temperature oil bath. Oxidation products were analyzed using Hewlett Packard gas chromatograph model 5890 A fitted with FID detector and a (30 m  $\times$  0.53 mm  $\times$  2.65  $\mu\text{m}$ ) HP-1 capillary column.

### 2.3. Preparations

#### 2.3.1. Preparation of nicotinoylchloride and isonicotinoylchloride

Nicotinoylchloride and isonicotinoylchloride were prepared using the method reported by Wingfield et al. [26]. For the synthesis of nicotinoylchloride, nicotinic acid (12.3 g, 100 mmol) was taken in a round bottom flask with 100 ml dry benzene, thionylchloride (6.0 ml, 80 mmol) was added to reaction mixture and refluxed for 12 h, protecting from moisture. The reaction mixture was used as such without any separation for later reactions. The same procedure was used for the preparation of isonicotinoylchloride except that isonicotinic acid (12.3 g, 100 mmol) was used in place of nicotinic acid.

#### 2.3.2. Preparation of $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$ (NiTaa)

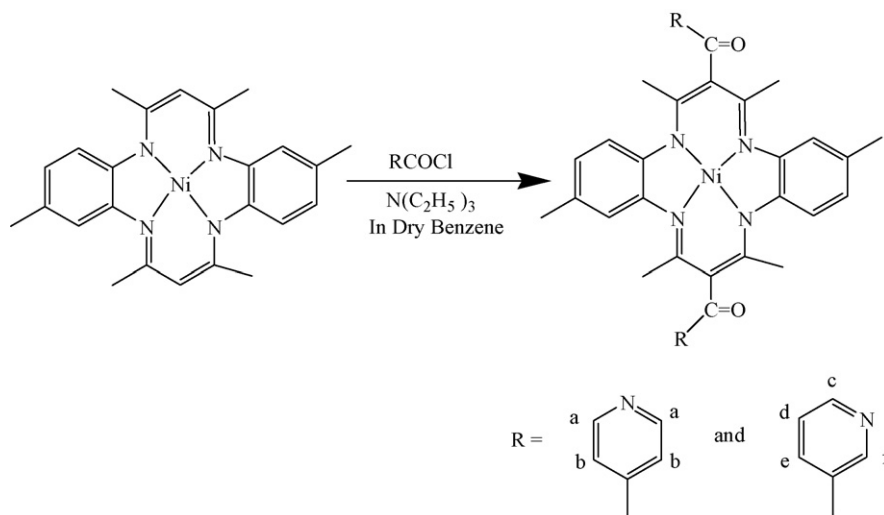
$[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$  was prepared following the method reported by Place et al. [27]. Nickel acetate (12.4 g, 50 mmol) and 3, 4 diaminotoluene (12.2 g, 100 mmol) were added to 120 ml *n*-butanol in 250 ml round bottom flask. The reaction mixture was refluxed on oil bath with constant stirring. After one and half hours acetylacetone (10.4 g, 100 mmol) was added and the reaction mixture was refluxed for 24 h. After cooling, 100 ml of methanol was added and the reaction mixture was kept overnight in a refrigerator. The crystals obtained were filtered and washed with methanol. Fine dark violet crystals were obtained. Yield 9.5 g (22%). m.p.  $>300^\circ\text{C}$ . Analyses found C, 67.29; H, 6.12; N, 13.01%.  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{Ni}$  calcd.: C, 67.16; H, 6.10; N, 13.05%. UV-vis (in chloroform  $\lambda_{\text{max}}$ ,  $\text{cm}^{-1}/\epsilon_{\text{max}}$ ,  $\text{L mol}^{-1} \text{cm}^{-1}$ ): 17065 (6214), 23310sh (9150), 25316 (36298), 29674 (8612), 37037 (32420), IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 2966w, 2913m, 2855m, 1579m, 1535s, 1462m, 1398vs, 1278m, 1209m, 1029s, 747m.  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ):  $\delta$  2.05(s 12H,  $\text{CH}_3$ ), 2.13 (s 6H, arom.  $\text{CH}_3$ ), 4.82 (s 2H methine) and 6.36–6.58 ppm (m 6H, arom.).

#### 2.3.3. Preparation of 7,16-dinicotinoyl $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$ (Ni-Nic)

$[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$  (2.5 g, 5.83 mmol) was dissolved in 50 ml dry benzene and the reaction mixture containing nicotinoylchloride (prepared in step 2.3.1) was mixed with it and then triethylamine (2.8 ml, 20 mmol) was added. The reaction mixture was refluxed for 12 h with constant stirring protecting from moisture. The reaction mixture was cooled down to room temperature and filtered. The filtrate was evaporated to dryness in a rotary evaporator and the product was washed with hot water till the washings become colourless. The product was then dried at  $80^\circ\text{C}$ , the dry residue was extracted in benzene and the benzene was evaporated in rotatory evaporator. The compound was purified by passage through a 20 cm  $\times$  2.5 cm alumina column eluting with benzene. Three green colored bands were observed. The first and second bands were minor and were discarded. The third green band was eluted with chloroform and the solvent was removed at reduced pressure. Yield 2.9 g (78.3%). m.p.  $>300^\circ\text{C}$ . Analyses found C, 67.92; H, 4.82; N, 13.03%.  $\text{C}_{36}\text{H}_{32}\text{N}_6\text{O}_2\text{Ni}$  calcd.: C, 67.61; H, 5.00; N, 13.15%. UV-vis (in chloroform  $\lambda_{\text{max}}$ ,  $\text{cm}^{-1}/\epsilon_{\text{max}}$ ,  $\text{L mol}^{-1} \text{cm}^{-1}$ ): 17094 (7012), 23365sh (13400), 25707 (35452), 30303 (10596), 37037 (52298), IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 2922m, 2851m, 1656s, 1579m, 1531s, 1446w, 1378vs, 1241s, 1023s, 739m. FAB mass ( $m/z$ )  $[\text{M}+1]^+$  641, 639.38 (calcd. molecular weight).  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ):  $\delta$  1.91(s 12H,  $\text{CH}_3$ ), 2.13 (s 6H, arom.  $\text{CH}_3$ ), 6.34–6.61 (m 6H, arom.), 7.56 (br s 2H (d)), 8.53 (br s 2H (e)), 8.86 (br s 2H (c)) and 9.44 ppm (br s 2H (f)) (Scheme 2).

#### 2.3.4. Preparation of 7,16-diisonicotinoyl $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$ (Ni-Iso)

The above procedure was followed for the preparation of 7,16-diisonicotinoyl $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$  except that



Scheme 2. Synthesis of tetraazamacrocycle complexes.

isonicotinoylchloride was used in place of nicotinoylchloride. Yield 2.75 g (74.3%). m.p. > 300 °C. Analyses found C, 67.81; H, 4.71; N, 13.00%.  $C_{36}H_{32}N_6O_2Ni$  calcd.: C, 67.63; H, 5.04; N, 13.15%. UV–vis (in chloroform  $\lambda_{max}$ ,  $cm^{-1}/\epsilon_{max}$ ,  $Lmol^{-1}cm^{-1}$ ): 17153 (7198), 23365sh (13050), 25707 (34485), 30212 (8510), 36900 (45068), IR (KBr pellet,  $\nu$   $cm^{-1}$ ): 2918s, 2850m, 1663s, 1594w, 1536s, 1450w, 1378vs, 1238s, 1021m, 725m. FAB mass ( $m/z$ )  $[M+1]^+$  640, 639.38 (calcd. molecular weight),  $^1H$  NMR (in  $CDCl_3$ ):  $\delta$  1.9(s 12H,  $CH_3$ ), 2.14 (s 6H, arom.  $CH_3$ ), 6.44–6.68 (m 6H, arom.) 8.86 (dd 4H (a)) and 8.00 ppm (dd 4H (b)) (Scheme 2).

#### 2.4. Catalyzed chemical oxidation of phenol

The catalytic hydroxylation was carried out in a 50 ml round bottom flask fitted with a water condenser. Phenol (0.59 g, 6.25 mmol) and 30%  $H_2O_2$  (0.71 g, 6.25 mmol) were mixed in 10 ml of doubly distilled water and the reaction mixture was heated with continuous stirring in an oil bath warmed to 80 °C. The reaction products were analyzed using a gas chromatograph by withdrawing small aliquots of the reaction mixture at specific times. The peaks in the chromatograms were identified as corresponding to catechol and hydroquinone by comparing the retention times with that of pure samples of catechol and hydroquinone and also using GC-MS. The gas chromatogram of reaction product showed no additional peaks other than phenol, catechol and hydroquinone. Polymeric material or other products, if any present in minor amounts, could not be detected by gas chromatography and were neglected. The reaction

was studied as a function of temperature, amount of oxidant and substrate, amount of catalyst, reaction time and effect of reaction media.

#### 2.5. Electrocatalytic oxidation of phenol

Electrocatalytic oxidation of phenol was investigated using linear sweep voltammetry technique. Electrocatalytic oxidation of phenol was carried out in double distilled water. Phosphate buffer 0.1 M (pH 7.3) was used as a supporting electrolyte. The linear sweep voltammograms were recorded for phenol ( $2 \times 10^{-3}$  M) on glassy carbon electrode and by glassy carbon electrode modified with NiTaa, Ni-Nic and Ni-Iso macrocycle complexes at the scan rate 200 mV/s using Ag/AgCl as reference electrode.

### 3. Results and discussion

#### 3.1. Synthesis and spectral studies

The electronic spectra of both the newly synthesized complexes and of the precursor complex are shown in Fig. 1. These complexes were found diamagnetic in nature at room temperature, indicating the square-planar environment around the metal ion, which is also supported by literature [28]. The absorption bands observed above the  $24,390\text{ cm}^{-1}$  are attributable to  $\pi \rightarrow \pi^*$  transitions within a macrocycle ring [29]. An extremely intense absorption band was observed at  $25,316\text{ cm}^{-1}$  in NiTaa. On acylation of NiTaa, this band shifts to a lower wavelength in acylated tetraazamacrocycle complexes. In Ni-Nic and Ni-Iso it was observed at  $25,707\text{ cm}^{-1}$ , i.e. at higher energy in acylated complexes. This appears to indicate that steric hindrance by nicotinoyl and isonicotinoyl groups produce strain in NiTaa skeleton [29]. Two absorption bands were observed in the electronic spectrum of the Ni-Iso complex at 17,153 and  $23,365\text{ cm}^{-1}$  while in Ni-Nic these bands were found at 17,094 and  $23,365\text{ cm}^{-1}$ . These bands may be assigned to d–d transitions of Ni(II), which corresponds to the bands of the precursor complex at 17,065 and  $23,310\text{ cm}^{-1}$ . The spectral behavior is consistent with that of square-planar coordination of Ni(II) [30]. The large molar absorbance of d–d transitions could be the result of intensity stealing from strong UV absorption bands [31].

The IR absorption bands are listed in Section 2. The macrocycle complexes Ni-Nic upon acylation show a strong band at  $1656\text{ cm}^{-1}$  due to C=O stretching mode along with three absorption bands at  $1531$  (N=C–C),  $1446$  (C=C) and  $1378$  (=C–H)  $cm^{-1}$  [32]. This three

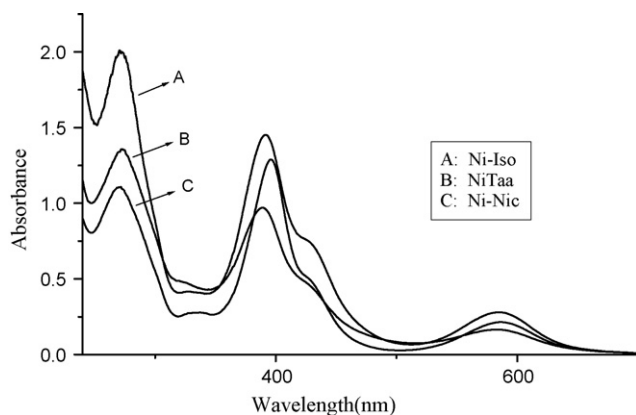


Fig. 1. Electronic spectra of Ni(II) tetraazamacrocycle complexes in  $CH_2Cl_2$ .

band pattern appeared in  $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$  at 1535, 1462 and  $1398\text{ cm}^{-1}$  while in case of Ni-Iso macrocycle complex the corresponding three band pattern was observed at 1536 ( $\text{N}=\text{C}-\text{C}$ ), 1450 ( $\text{C}=\text{C}$ ) and  $1378\text{ cm}^{-1}$  and  $\text{C}=\text{O}$  stretching mode at  $1663\text{ cm}^{-1}$ .

The precursor macrocycle complex  $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$  exhibited four NMR signals at  $\delta$  2.05 (12H,  $\text{CH}_3$ ),  $\delta$  2.13 (6H, aromatic  $\text{CH}_3$ ),  $\delta$  4.8 (2H, methine),  $\delta$  6.36–6.58 ppm (6H, aromatic) in  $\text{CDCl}_3$ . All these signals except the methine proton signals also appeared in Ni-Nic and Ni-Iso complexes. The methine proton signal of the 7 and 16 positions disappeared after the acylation and pyridine proton signals are observed in the n.m.r. spectra at  $\delta$  7.30–9.50 ppm. The substituted pyridine proton signals have shifted down field by the deshielding effect of benzene rings. In Ni-Nic complex pyridine proton signals were observed at 7.56 (brs 2H (d)), 8.53 (brs 2H (e)), 8.86 (brs 2H (c)) and 9.44 ppm (brs 2H (f)) while in Ni-Iso complex they appeared at 8.86 (dd 4H (a)) and 8.00 ppm (dd 4H (b)) (as shown in Scheme 2), also the (12H,  $\text{CH}_3$ ) proton signals upon acylation showed an upfield shift because these twelve methyl protons lie in the shielding zone produced by the magnetic anisotropy of the pyridine rings.

This type of tetraazamacrocycle attains saddle shaped geometry due to the presence of two phenyl rings. Due to the square-planar saddle type geometry, the vacant axial sites present in such macrocycle complexes facilitate weak coordination with small molecule or anions [3,4,33,34] with metal center.

### 3.2. Electrochemistry and electrocatalysis

Cyclic voltammograms of all the three macrocycle complexes were recorded in dry acetonitrile/benzene (1:1, v/v) mixture using a glassy carbon (GCE) working microelectrode and  $\text{Ag}/\text{AgCl}$  reference electrode. In the anodic scan the precursor macrocycle complex NiTaa exhibits two irreversible oxidation peaks at 0.47 V and 1.11 V and in cathodic scan one reduction peak at  $-1.88\text{ V}$  versus  $\text{Ag}/\text{AgCl}$  as reported by Rillema and co-workers [35]. Ni-Nic and Ni-Iso both exhibit two oxidation peaks at higher potentials at 0.78 V and 0.74 V respectively in contrast to the precursor  $[\text{Ni}\{\text{Me}_4(4\text{-MeBzo})_2[14]\text{tetraeneN}_4\}]$  macrocycle complex. First oxidation process in both the cases is an electrochemically reversible redox process (Fig. 2). It seems to be due to oxidation of the cation  $[\text{Ni-Nic}]^+$  and  $[\text{Ni-Iso}]^+$  [36] while the second oxidation peak in both the cases was irreversible and were observed

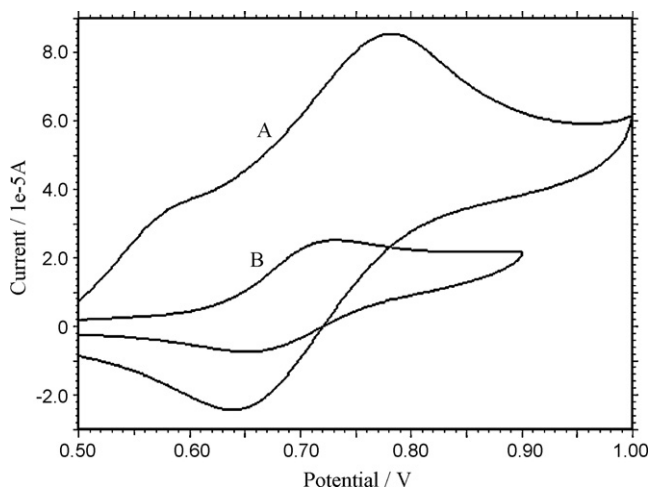


Fig. 2. Cyclic voltammograms of Ni-Nic (A) and Ni-Iso (B) in acetonitrile/benzene (1:1, v/v) mixture at GCE in presence of 0.1 M TEAP supporting electrolyte.

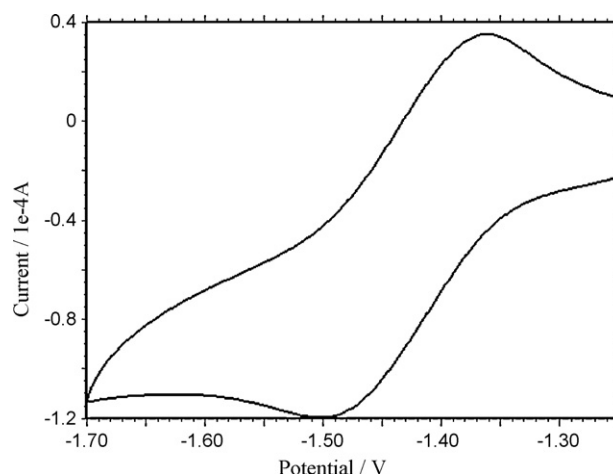


Fig. 3. Cyclic voltammograms Ni-Iso in acetonitrile/benzene (1:1, v/v) mixture at GCE in presence of 0.1 M TEAP supporting electrolyte.

at 1.36 V and 1.38 V versus  $\text{Ag}/\text{AgCl}$ , respectively. This is due to  $\text{Ni}^{+2}/\text{Ni}^{+3}$  [35–37]. In the cathodic sweep, Ni-Nic and Ni-Iso both exhibited two reduction peaks while precursor macrocycle complex showed only one peak. First reduction peak in Ni-Nic observed at  $-1.67\text{ V}$  was found to be irreversible while in case of Ni-Iso the peak observed at  $-1.50\text{ V}$  corresponds to a reversible redox process (Fig. 3). These reductions must be associated with the acylated groups [36,38]. Ni-Nic and Ni-Iso exhibit second reduction peaks at  $-1.85\text{ V}$  and  $-1.95\text{ V}$  versus  $\text{Ag}/\text{AgCl}$  which were irreversible and associated with metal center, i.e.  $\text{Ni}^{+2}/\text{Ni}^{+1}$  [37]. Fig. 4 shows linear sweep voltammograms of  $2 \times 10^{-3}\text{ M}$  phenol in double distilled water, 0.1 M phosphate buffer (pH = 7.3) as supporting electrolyte recorded at a bare glassy carbon electrode (A), glassy carbon electrode modified with Ni-Nic (C) and with Ni-Iso (B). Phenol does not show any oxidation up to  $E=2.0\text{ V}$  versus  $\text{Ag}/\text{AgCl}$  on glassy carbon electrode in acetonitrile solution [4], even in the presence of either Ni-Nic or Ni-Iso tetraazamacrocycle complexes. However, on adding NaOH solution the voltammogram of the solution changed appreciably due to formation of phenoxide ion which showed an irreversible oxidation peak. Solution of phenol in doubly distilled water with phosphate buffer (pH 7.3) as supporting electrolyte exhibited oxidation peak at 0.57 V at bare

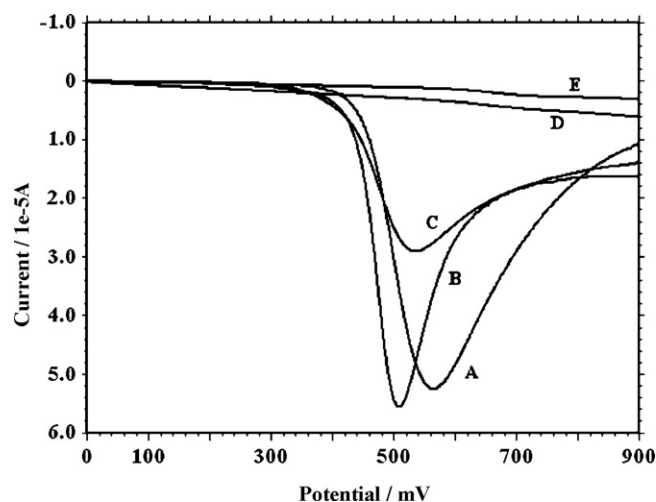


Fig. 4. Linear sweep voltammograms of  $2 \times 10^{-3}\text{ M}$  phenol at bare GCE (A), Ni-Iso modified GCE (B), Ni-Nic modified GCE (C), Ni-Nic modified GCE blank (D) and Ni-Iso modified GCE blank (E) in double distilled water in presence of 0.1 M phosphate buffer of pH 7.3 as supporting electrolyte.



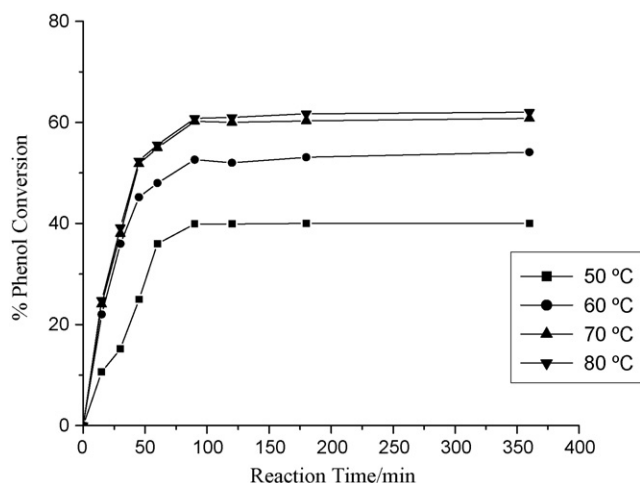


Fig. 5. Effect of temperature on the oxidation of phenol.

glassy carbon electrode. When glassy carbon electrode was modified by the complex Ni-Nic, oxidation of phenol was observed at a lower potential of 0.52 V while in case of Ni-Iso it was observed at 0.51 V shifting to 0.06 V at lower potential, with enhanced peak current.

### 3.3. Catalytic activity

The hydroxylation of phenol in aqueous medium was carried out using three different catalysts NiTaa, Ni-Nic and Ni-Iso. Phenol (0.59 g, 6.25 mmol) and 30%  $H_2O_2$  (0.71 g, 6.25 mmol) were mixed in 10 ml of doubly distilled water. To this 20 mg of Ni-Nic, 20 mg Ni-Iso and 14 mg of NiTaa catalyst were added in three different runs. The reaction mixture was heated for 6 h with continuous stirring in an oil bath at 80 °C. The progress of the reaction was monitored by gas chromatography. The two expected products namely catechol and hydroquinone were observed along with phenol in all three cases. Polymeric material or other products, if any present in minor amounts, could not be detected by gas chromatography. It was found that the Ni-Iso, Ni-Nic and NiTaa catalysts gives 60.5%, 52.0% and 27.0% conversion of phenol respectively under similar conditions. All three macrocycle complex catalysts are more selective for catechol formation. To determine suitable reaction conditions for maximum conversion, studies of various reaction parameters were performed as described in the following sections. Since Ni-Iso catalyst gives the maximum conversion of phenol, it is used as a representative catalyst for further studies.

#### 3.3.1. Effect of temperature

The performance of the catalyst Ni-Iso was monitored at four different temperatures viz. 50, 60, 70 and 80 °C in four different reaction sets. Phenol (0.59 g, 6.25 mmol), 30%  $H_2O_2$  (0.71 g, 6.25 mmol) were taken in 10 ml of doubly distilled water and 20 mg of catalyst Ni-Iso was added to it and the reaction was run at each temperature over a period of 6 h. The results are shown in Fig. 5 and Table 1. It is seen that at 70 °C there is 60.2% conversion of phenol. On increasing the temperature to 80 °C no significant change was observed, whereas the percentage of phenol conversion at 50 and 60 °C were found to be 40.0% and 53.9%, respectively. In all cases the maximum conversion was reached within the first 90 min and thereafter only a negligible change was observed. The turn over frequency of the reaction at 70 and 80 °C were practically the same as seen from Table 1. At 70 °C temperature the catechol:hydroquinone ratio is also highest. So 70 °C is the optimal temperature for higher phenol conversion as well as catechol formation.

Table 1

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

Reaction temperature (°C)	Phenol conversion (%)	TOF <sup>b</sup> (h <sup>-1</sup> )	Product selectivity (%)		CAT/HQ ratio
			CAT <sup>c</sup>	HQ <sup>d</sup>	
50	40.0	13.4	75.3	25.6	2.9
60	53.9	18.0	82.9	17.1	4.8
70	60.2	20.1	87.1	12.9	6.8
80	60.5	20.2	87.1	12.9	6.8

<sup>a</sup> Reaction conditions: phenol = 0.59 g; 30%  $H_2O_2$  = 0.71 g; catalyst Ni-Iso = 0.020 g; reaction time = 6 h.

<sup>b</sup> TOF = moles of product formed per mole of catalyst per hour.

<sup>c</sup> Catechol.

<sup>d</sup> Hydroquinone.

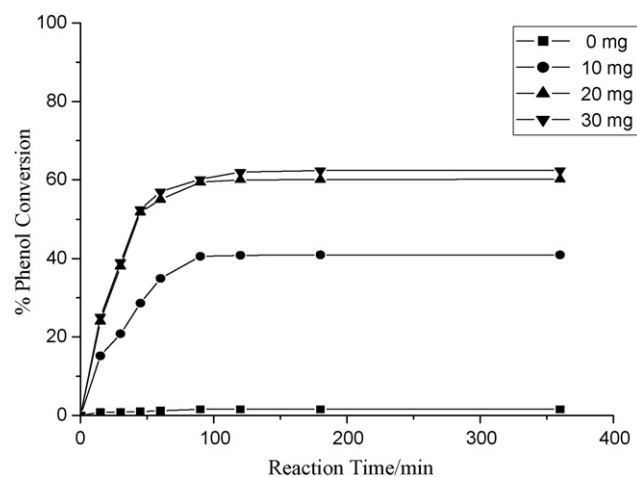


Fig. 6. Effect of amount of catalyst on the oxidation of phenol.

#### 3.3.2. Effect of amount of catalyst

Amount of catalyst has a significant effect on the percentage conversion of phenol. Phenol (0.59 g, 0.006 mol) and 30%  $H_2O_2$  (0.71 g, 0.006 mol) were dissolved in 10 ml of double distilled water. Three different amounts of catalyst Ni-Iso viz. 10 mg (0.016 mmol), 20 mg (0.032 mmol) and 30 mg (0.048 mmol) were used to study the effect of the amount of catalyst on percent conversion of phenol. Reaction was carried out at 70 °C in all three cases. A reaction without catalyst under similar condition showed 1.9% conversion of phenol. From the results as shown in Fig. 6 and Table 2, it is seen that 10 mg catalyst gives 40.9% conversion of phenol and that on with 20 mg of catalyst the percentage conversion of phenol increased to 60.2%. Further increase in amount of catalyst to 30 mg resulted in only slight change in percentage conversion of the phenol, and so 20 mg of catalyst is found optimal.

#### 3.3.3. Effect of $H_2O_2$ concentration

Effect of  $H_2O_2$  concentration on the oxidation of phenol was studied and the results are shown in Fig. 7 and Table 3. Three different sets of molar ratios of hydrogen peroxide to phenol viz. 0.5:1,

Table 2

Effect of the amount of catalyst on the oxidation of phenol.

Catalyst weight (mg)	Phenol conversion after 6 h (%)	Phenol/catalyst molar ratio	TOF (h <sup>-1</sup> )
0	1.9	–	–
10	40.9	404.9	27.3
20	60.2	202.4	20.1
30	62.4	135.0	13.9

Reaction conditions: phenol = 0.59 g; 30%  $H_2O_2$  = 0.71 g; T = 70 °C; reaction time = 6 h.

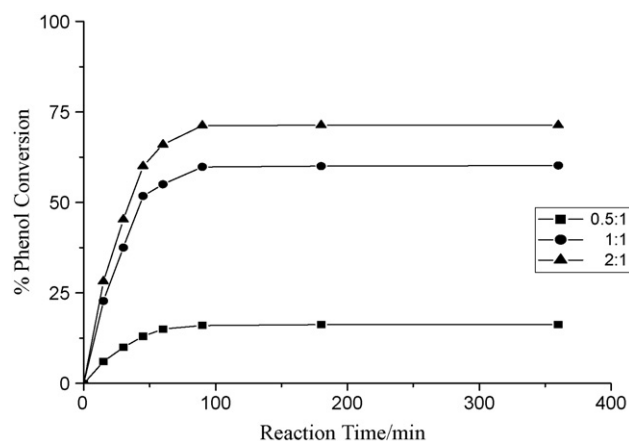


Fig. 7. Effect of  $\text{H}_2\text{O}_2$ :phenol molar ratio on the oxidation of phenol.

1:1, and 2:1 were taken in 10 ml double distilled water with a fixed amount of 6.25 mmol of phenol and 20 mg of catalyst Ni-Iso. The reaction was carried out at  $70^\circ\text{C}$  for 6 h. When the  $\text{H}_2\text{O}_2$ : phenol molar ratio was 2:1 and 1:1 the percentage conversion of phenol was observed to be 71.2% and 60.2%, respectively. In case of  $\text{H}_2\text{O}_2$ : phenol molar ratios of 2:1 and 1:1, the percentage  $\text{H}_2\text{O}_2$  efficiency were 35.6% and 60.2%, respectively. In case of 0.5:1 molar ratio, the percentage conversion of phenol was 16.3% and the percentage  $\text{H}_2\text{O}_2$  efficiency was 32.6%. The product selectivity of catechol increased with decrease in molar ratio of  $\text{H}_2\text{O}_2$ :phenol. When the  $\text{H}_2\text{O}_2$ :phenol molar ratio was changed from 1:1 to 2:1 the increase in conversion of phenol was only 10%. On the basis of these results it can be concluded that on balancing higher conversion of phenol and  $\text{H}_2\text{O}_2$  efficiency, 1:1 molar ratio of  $\text{H}_2\text{O}_2$ :phenol was optimum.

### 3.3.4. Effect of reaction time

The effect of reaction time on the catalyzed hydroxylation of phenol by  $\text{H}_2\text{O}_2$  in aqueous medium was studied. Phenol (0.59 g, 6.25 mmol), 30%  $\text{H}_2\text{O}_2$  (0.71 g, 6.25 mmol) and Ni-Iso catalyst (20 mg) were taken in 10 ml double distilled water. Reaction was carried out at  $70^\circ\text{C}$  for 18 h with continuous stirring. It was found that conversion of phenol increases rapidly in the beginning of reaction and a conversion of 60.2% was achieved in first 90 min. No appreciable change in conversion of phenol was recorded on running the reaction for 6 h. Selectivity of catechol and hydroquinone were found to be 87.1% and 12.9%. When the reaction was allowed to continue, 61.1% conversion was observed at the end of 18 h and the selectivity for catechol and hydroquinone remained unchanged.

### 3.3.5. Effect of reaction media on oxidation of phenol

Effect of reaction media on oxidation of phenol was investigated in acidic and alkaline media. Phenol (0.59 g, 6.25 mmol), 30%  $\text{H}_2\text{O}_2$  (0.71 g, 6.25 mmol) and 20 mg of Ni-Iso catalyst were put in 10 ml double distilled water and the reaction was carried out in presence of (0.1 M) glacial acetic acid and (0.1 M) ammonia at  $70^\circ\text{C}$ . The results are shown in Fig. 8. It was found that the reaction was

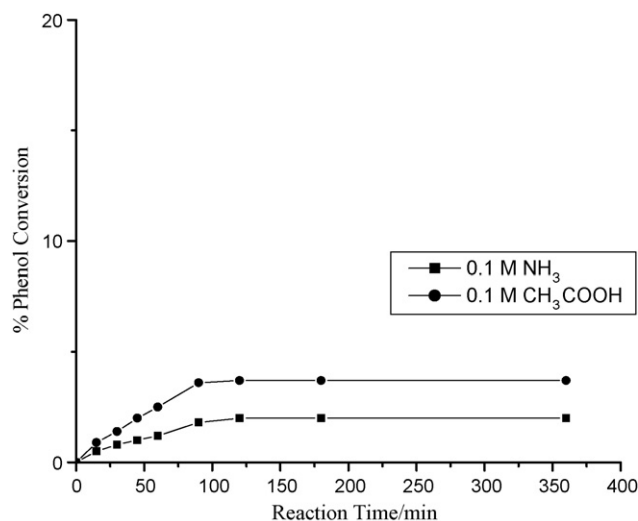


Fig. 8. Effect of reaction medium on the oxidation of phenol.

almost stopped in alkaline medium whereas in the acidic medium reaction progress was very slow. The poor reaction progress in acidic medium is probably due to protonation of phenoxide ion, while in case of alkaline medium ammonia might weakly coordinate with the metal center blocking the diaxial sites of metal center of catalyst.

### 3.4. Test for heterogeneity and recyclability

The recyclability of the catalysts has been tested in a typical run, where after a contact time of 6 h, the reaction mixture was filtered. The used Ni-Iso catalyst was activated by stirring the catalyst with acetonitrile for 1 h followed by filtration. This process is repeated twice and the catalyst was dried at  $90^\circ\text{C}$  in an oven. It was reused for a run under similar conditions. It showed nearly equal catalytic activity for the first cycle and there was a very minor loss for the second cycle. Electronic and IR spectra of used and fresh catalyst were also nearly the same. All these studies suggest that the catalyst is sufficiently stable and recyclable. The filtrate collected after separating the used catalyst was placed in the reaction flask and the reaction was continued after adding fresh  $\text{H}_2\text{O}_2$  for another 6 h. No significant change was observed in the percentage conversion of phenol and no metal content was found in the filtrate of reaction mixture by AAS. This showed that there was no metal leaching during the reaction and the reaction was heterogeneous in nature.

### 3.5. Possible reaction pathway

To establish the possible path of reaction, a  $10^{-5}$  M solution of tetraazamacrocycle complex Ni-Iso in methanol (prepared by first dissolving in chloroform and diluting by methanol) was titrated against methanolic solution of 30%  $\text{H}_2\text{O}_2$ , and the progress

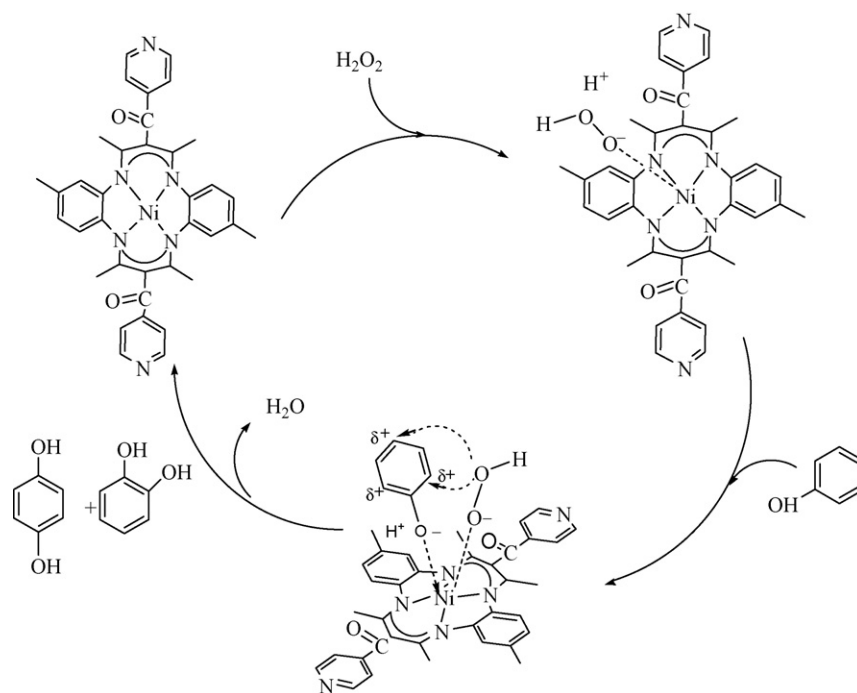
Table 3

Influence of  $\text{H}_2\text{O}_2$ : $\text{C}_6\text{H}_5\text{OH}$  molar ratio on the phenol conversion, percent  $\text{H}_2\text{O}_2$  efficiency, and product selectivity.

$\text{H}_2\text{O}_2$ : $\text{C}_6\text{H}_5\text{OH}$ molar ratio	Phenol conversion (%)	$\text{H}_2\text{O}_2$ efficiency <sup>a</sup> (%)	Product selectivity (%)	
			CAT	HQ
0.5:1	16.3	32.6	92.1	7.9
1:1	60.2	60.2	87.1	12.9
2:1	71.2	35.6	84.9	15.1

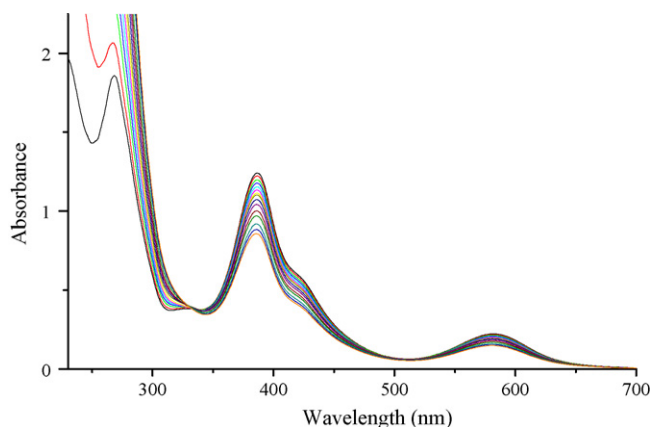
Reaction conditions: catalyst Ni-Iso = 0.020 g;  $T = 70^\circ\text{C}$ ; reaction time = 6 h.

<sup>a</sup>  $\text{H}_2\text{O}_2$  efficiency (%) = (mol of  $\text{H}_2\text{O}_2$  used in product formation/mol of  $\text{H}_2\text{O}_2$  added)  $\times$  100.



**Scheme 3.** Proposed mechanism for catalyzed phenol oxidation in presence of  $\text{H}_2\text{O}_2$ .

of reaction was monitored by UV–visible spectrophotometry. With addition of the methanolic solution of 30%  $\text{H}_2\text{O}_2$  to the methanolic solution of Ni-Iso the intensity of the 17,153, 23,365 and  $25,707\text{ cm}^{-1}$  peak decreased, while peaks at 30,212 and  $36,900\text{ cm}^{-1}$  gradually increased in intensity. The spectral changes are shown in Fig. 9. An isobestic point was found at  $30,120\text{ cm}^{-1}$ . The decrease in the intensity of the peak at  $17,153\text{ cm}^{-1}$  suggests that the Ni-Iso interacts with  $\text{H}_2\text{O}_2$  and produces the active species (Iso-Ni-OOH<sup>-</sup>). This active species subsequently interacts with phenol and produces the intermediate (Iso-Ni-phenol-OOH<sup>-</sup>) as shown in Scheme 3. The intermediate facilitates the attack of OOH<sup>-</sup> at the ortho and para position of phenol producing catechol and hydroquinone. The intermolecular oxidation–reduction reaction between the hydrogen peroxide and phenol seems to be an intramolecular electron transfer reaction in the intermediate species (phenol-Ni-Iso-OOH<sup>-</sup>), which decreases the activation energy for the oxidation of phenol and the rate is enhanced significantly [39–42].



**Fig. 9.** Spectral change during titration of Ni-Iso with 30%  $\text{H}_2\text{O}_2$ .

#### 4. Conclusions

Tetraazamacrocycle complexes of Ni(II) have been synthesized by acylation of nicotinoylchloride and isonicotinoylchloride. The synthesized complexes were characterized and their catalytic activity towards wet chemical oxidation of phenol using  $\text{H}_2\text{O}_2$  as oxidant has been investigated. All the tetraazamacrocycle complexes catalyze the oxidation of phenol, yielding catechol and hydroquinone as oxidation products. The performance of Ni-Iso catalyst was found to be superior to that of Ni-Nic and NiTaa catalysts. The oxidation of phenol is highly selective with catechol 87.1% constituting the major product. The effects of temperature, amount of catalyst, reaction time, effect of oxidant and substrate concentration and effect of reaction media on the oxidation were studied. Based on the coordination behavior of the complex a possible mechanism has been proposed for the catalytic oxidation process (Scheme 3). Catalyst Ni-Iso is stable, recyclable and free from metal leaching. It can be effectively used as a heterogeneous catalyst.

#### Acknowledgements

One of the authors (VKB) is thankful to the Ministry of Human Resource and Development (MHRD), New Delhi, India for providing funds to undertake the work and also the Head, RSIC CDRI, Lucknow, India for recording mass spectra of the complexes. VKB also wishes thanks to Dr. R.K. Peddinti, Department of Chemistry, IIT Roorkee for his kind support.

#### References

- [1] J. Połtowicz, K. Pamin, J. Haber, *J. Mol. Catal. A: Chem.* 257 (2006) 154–157.
- [2] O. Rothhaus, S.L. Roy, A. Tomas, K.M. Barkigia, I. Artaud, *Inorg. Chim. Acta* 357 (2004) 2211–2217.
- [3] V.K. Bansal, R. Kumar, R. Prasad, S. Prasad, Niraj, *J. Mol. Catal. A: Chem.* 284 (2008) 69–76.
- [4] H.S. Abbo, S.J.J. Titinchi, S. Chand, R. Prasad, *J. Mol. Catal. A: Chem.* 218 (2004) 125–132.
- [5] K.O. Xavier, J. Chackoa, K.K.M. Yusuff, *Appl. Catal. A: Gen.* 258 (2004) 251–259.

- [6] M.R. Maurya, A.K. Chandrakar, S. Chand, *J. Mol. Catal. A: Chem.* 278 (2007) 12–21.
- [7] M. Salavati-Niasari, M. Shakouri-Arani, F. Davar, *Micropor. Mesopor. Mater.* 117 (2008) 77–85.
- [8] M.R. Maurya, A.K. Chandrakar, S. Chand, *J. Mol. Catal. A: Chem.* 270 (2007) 225–235.
- [9] K.P. Borujeni, A.R. Massah, *React. Funct. Polym.* 66 (2006) 1126–1131.
- [10] G. Li, L. Chen, J. Bao, T. Li, F. Mei, *Appl. Catal. A: Gen.* 346 (2008) 134–139.
- [11] K.P. Borujeni, B. Tamami, *Catal. Commun.* 8 (2007) 1191–1196.
- [12] T. Punniyamurthy, S.J.S. Kalra, J. Iqbal, *Tetrahedron Lett.* 36 (1995) 8497–8500.
- [13] (a) A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez, F. García-Ochoa, *Appl. Catal. B: Environ.* 39 (2002) 97–113;  
(b) A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. García-Ochoa, *Appl. Catal. B: Environ.* 61 (2005) 323–333.
- [14] M.A. Brimble, L.J. Duncalf, S.J. Phythiom, *J. Chem. Soc. Perkin Trans. 1* 9 (1997) 1399–1403.
- [15] (a) C. Skepalik, *Ger. Offen.*, 2138735 (1973).;  
(b) S.W. Brown, *Br. Patent Appl.*, 913323 (1991).
- [16] D.W. Hansen, R. Pappo, R.B. Garland, *J. Org. Chem.* 53 (1988) 4244–4253.
- [17] S. Itoh, M. Ogino, S. Haranou, T. Terasaka, T. Ando, M. Komatsu, Y. Ohshiro, S. Fukuzumi, K. Kano, K. Takagi, T. Ideka, *J. Am. Chem. Soc.* 17 (1995) 1485–1493.
- [18] I.A. Salem, *Appl. Catal. B: Environ.* 28 (2000) 153–162.
- [19] S. Ray, S.F. Mapolie, J. Darkwa, *J. Mol. Catal. A: Chem.* 267 (2007) 143–148.
- [20] M. Salavati-Niasari, M. Bazarganipour, *Catal. Commun.* 7 (2006) 336–343.
- [21] M.R. Maurya, S.J.J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* 201 (2003) 119–130.
- [22] P.S. Chittilappilly, N. Sridevi, K.K.M. Yusuff, *J. Mol. Catal. A: Chem.* 286 (2008) 92–97.
- [23] I.U. Castro, F. Stüber, A. Fabregat, J. Font, A. Fortuny, C. Bengoa, *J. Hazard. Mater.* 163 (2009) 809–815.
- [24] S. Yang, X. Li, W. Zhu, J. Wang, *C. Descorme, Carbon* 46 (2008) 445–452.
- [25] M. Salavati-Niasari, M. Bazarganipour, *Appl. Surf. Sci.* 255 (2008) 2963–2970.
- [26] H.N. Wingfield, W.R. Harlan, H.R. Hamner, *J. Am. Chem. Soc.* 75 (1953) 4364.
- [27] D.A. Place, G.P. Ferrara, J.J. Harland, J.C. Dabrowiak, *J. Heterocycl. Chem.* 17 (1980) 439–443.
- [28] H. Schumann, *Z. Naturforsch. B: Chem. Sci.* 51 (1996) 989–998.
- [29] K. Sakata, M. Itoh, *J. Heterocycl. Chem.* 29 (1992) 921–926.
- [30] (a) B.N. Figgis, *Introduction to Ligand Fields*, Wiley, New York, 1966;  
(b) A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984.
- [31] W.P. Schammel, L.L. Zimmer, D.H. Busch, *Inorg. Chem.* 19 (1980) 3159–3167.
- [32] K. Sakata, O. Terada, T. Honda, M. Hashimoto, *React. Inorg. Met.-Org. Chem.* 23 (1993) 373–381.
- [33] J. Eilmes, M. Ptaszeka, K. Wozniak, *Polyhedron* 21 (2002) 7–17.
- [34] M. Villagran, J. Costamagna, J.H. Zagal, G. Cardenas-jiron, M. Paez, *J. Coord. Chem.* 59 (2006) 1467–1475.
- [35] C.L. Baily, R.D. Bereman, D.P. Rillema, R. Nowak, *Inorg. Chem.* 23 (1984) 3956–3960.
- [36] B.K. Daszkiewicz, J. Taraszewska, K. Zieba, A. Makal, K. Wozniak, *Eur. J. Inorg. Chem.* 16 (2004) 3335–3344.
- [37] J.C. Dabrowiak, D.P. Fisher, F.C. McElroy, D.J. Macero, *Inorg. Chem.* 18 (1979) 2304–2307.
- [38] R.R. Amaro, R. Perez, V. Lopez, J.J. Ruiz, *J. Electroanal. Chem.* 278 (1990) 307–322.
- [39] J. Zhang, Y. Tang, J.Q. Xie, J.Z. Li, W. Zeng, C.W. Hu, *J. Serb. Chem. Soc.* 70 (2005) 1137–1146.
- [40] J.Q. Xie, J.Z. Li, X.G. Meng, C.W. Hu, X.C. Zeng, *Trans. Met. Chem.* 29 (2004) 388–393.
- [41] K.C. Gupta, A.K. Sutar, *React. Funct. Polym.* 68 (2008) 12–16.
- [42] J.Z. Li, J.Q. Xie, W. Zeng, X.Y. Wei, B. Zhou, X.C. Zeng, S.Y. Qin, *Trans. Met. Chem.* 29 (2004) 488–494.