

# Catalytic hydroxylation of phenol using immobilized late transition metal salicylaldimine complexes

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## Abstract

Immobilized late transition metal complexes based on salicylaldimine ligands were used as catalysts in the wet air hydroxylation of phenol in the presence of hydrogen peroxide. Three metals, viz. cobalt, nickel and copper, and two different kinds of supports, namely, amorphous silica and mesoporous MCM-41, were employed. The effect of pH on the hydroxylation process was also investigated. It was observed that the regioselectivity of the hydroxylation process strongly depends on the kind of support employed.

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## 1. Introduction

Catechol and hydroquinone have a very wide range of applications, ranging from pharmaceuticals to polymers, photographic and agrochemical materials. Wet air oxidation of phenol is a well-known synthetic route to produce these dihydroxybenzenes. Most of the common techniques for wet oxidation of phenol involve the use of hydrogen peroxide as an oxidant. The advantage of hydrogen peroxide over other potential oxidants is its relative stability. In addition, hydrogen peroxide is a relatively strong oxidant.

Examples of homogeneous processes known to produce dihydroxybenzenes are the Rhône-Poulenc process [1], where the oxidation of phenol is catalyzed by strong mineral acids, or the Hamilton process [2], where Fenton reagent is used as a catalyst. These processes, being homogeneous in nature, face difficulties with continuous operation, catalyst recovery and separation. The use of heterogeneous catalysts can eliminate such difficulties. Titanium silicate (TS-1), which is a titanium containing zeolite, is one of such heterogeneous catalysts [3]. One of the advantages of TS-1 is higher para selectivity, which is attributed to the

shape selectivity of the catalyst [4–10]. Another advantage of this catalyst is the higher phenol conversion and the low amount of tar formation. However, the difficult preparative method for TS-1 makes it a less desirable option for phenol hydroxylation. Several other heterogeneous systems have been tried for the hydroxylation of phenol. These include metals encapsulated within zeolites [11–21] and metals encapsulated in pillared clays [22]. Several metals, such as iron, cobalt, nickel and copper have been tried as catalysts in the phenol hydroxylation processes. All of the above-mentioned heterogeneous systems involve the physical absorption of metal salts or metal complexes on the inorganic support.

In this paper we report on salicylaldimine complexes of cobalt, nickel and copper chemically immobilized on two different kinds of materials, namely, amorphous silica and mesoporous MCM-41. These systems were evaluated as catalysts in phenol hydroxylation over a range of pH values. The effect of the nature of the support on catalyst performance was also evaluated.

## 2. Experimental

### 2.1. Materials

All the chemicals were procured from Sigma–Aldrich Ltd. unless otherwise mentioned. The solvents ethanol, dichloro-

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methane and toluene were procured from Kimix Ltd., South Africa and were dried using appropriate drying agents. Amorphous silica gel (Davisil, Grade 710) was procured from Sigma–Aldrich. MCM-41 was synthesized using a reported method [23] employing tetraethylorthosilicate as the starting material and cetyltrimethylammonium bromide as the template.

## 2.2. Techniques

$^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  using a Varian XR200 spectrometer. Sample signals are relative to the resonance of residual protons in the solvent. Chemical analysis for cobalt, nickel and copper was performed using atomic absorption spectroscopy on a Pye Unicam 9100 atomic absorption spectrophotometer. Powder X-ray diffraction patterns were recorded on a Bruker-AXS diffractometer using a  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5409 \text{ \AA}$ ) and a graphite monochromator at Ithemba Laboratories, Somerset West, South Africa. The samples were scanned in the  $2\theta$  range of  $2\text{--}10^\circ$ , with  $\Delta 2\theta = 0.01$ . Diffused Reflectance FTIR spectra were recorded using a Perkin-Elmer Paragon 1000 PC spectrometer. The BET surface area was analyzed using a Tristar 3000 micromeritics Surface Area and Porosity Analyzer at the Chemical Engineering Department of the University of Cape Town, South Africa. Prior to the measurement, the samples were degassed at  $90^\circ\text{C}$  for 1 h and ramped to  $165^\circ\text{C}$  over 1 h at a pressure of 70 bar. The analysis bath was kept at 77 K. Analysis of the catalysis products was carried out on a HP 1090 Liquid Chromatograph. A ZORBAX<sup>®</sup> SB-C18 column of dimension  $4.6 \text{ mm} \times 150 \text{ mm}$  was used to analyze the residual phenol, and the resulting catechol and hydroquinone in the reaction mixture. The mobile phase used was a mixture of 0.1% formic acid solution and acetonitrile.

## 2.3. Synthesis of the salicylaldiminato complex

Synthesis of the ligand was performed using a reported method with slight modifications [24,25]. Aminopropyl triethoxysilane (2.21 g, 10 mmol), dissolved in 10 mL of dry ethanol, was added to salicylaldehyde (1.22 g, 10 mmol). To it 30 mL dry ethanol was added. The resulting mixture was refluxed for 2 h. The solvent was removed in *vacuo*. The resulting viscous orange oil was dissolved in dichloromethane and washed with two 10 mL portions of water. The organic layer was separated and then dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off and the solvent was removed to obtain the salicylaldimine ligand (A). Yield = 68%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.68$  (t,  $^3J_{\text{H,H}} = 8.4 \text{ Hz}$ , 2H, Si- $\text{CH}_2$ ), 1.23 (t,  $^3J_{\text{H,H}} = 7.0 \text{ Hz}$ , 9H, Si- $\text{OCH}_2\text{CH}_3$ ), 1.82 (t,  $^3J_{\text{H,H}} = 7.0 \text{ Hz}$ , 2H,  $\text{NCH}_2$ ), 3.627 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.82 (q,  $^3J_{\text{H,H}} = 7.0 \text{ Hz}$ , 6H, Si- $\text{OCH}_2$ ), 6.93 (m, 2H, Ar), 7.29 (m, 2H, Ar), 8.33 (s, 1H,  $\text{N}=\text{CH}$ ). IR ( $\text{cm}^{-1}$ , chloroform) 1637 ( $\nu$  C=N), 1267 ( $\nu$  C-O), 1475 ( $\delta$   $\text{CH}_3_{\text{as}}$ ), 1380 ( $\delta$   $\text{CH}_3_{\text{s}}$ ). The cobalt, nickel and the copper salicylaldimine complexes were prepared using a reported method [24].

## 2.4. Immobilization of the metal complexes

The solid supports (MCM-41 and amorphous silica, Davisil 710) were degassed under vacuum at  $100^\circ\text{C}$  overnight prior to use. The solid support (1.0 g) was transferred into a 100 mL round bottomed flask and to it 100 mg ( $\sim 0.14 \text{ mmol}$ ) of the salicylaldimine complex followed by dry toluene (20 mL) were added. The slurry was refluxed for 4 h. At the end of the refluxing period, the solid was filtered and washed repeatedly first with toluene ( $5 \times 20 \text{ mL}$ ) followed by copious amounts of dichloromethane until the washing were completely colourless. The solids obtained were collected and dried under vacuum at room temperature for 10 h [26]. The metal loading of the various immobilized catalysts was determined using Atomic-Absorption Spectroscopy.

## 2.5. Phenol hydroxylation experiments

Batch reactions were carried out using a Radley's Discovery Technologies 12 place Heated Carousel Reaction Station fitted with a Reflux unit as well as a gas distribution system. The reactions were performed in 45 mL glass reactors using deionized water buffered at the appropriate pH as a solvent. Requisite amounts of the catalyst giving 0.01 mmol metal, was added to the glass reactor, followed by 1 mmol of phenol and 10 mL of the buffered solvent, which had previously been saturated with oxygen. The resulting mixture was stirred at  $110^\circ\text{C}$  for 15 min under an oxygen blanket, after which 1 mmol of 6%  $\text{H}_2\text{O}_2$  was added to the solution. The reaction was allowed to continue for 6 h at  $110^\circ\text{C}$  under a constant flow of oxygen. After completion of the reaction, the products formed were analyzed by HPLC after diluting the sample a 100 times with deionized water. Samples were filtered through a nylon syringe filter membrane of  $0.45 \mu\text{m}$ , thickness prior to injection onto the HPLC column.

## 3. Result and discussion

In the current study, the effect of two different types of support systems were investigated, viz. amorphous silica (Davisil 710) and mesoporous MCM-41 using three different metal salicylaldimine complexes, namely, cobalt, nickel and copper (Table 1, Scheme 1). Liquid phase hydroxylations of phenol were carried out in conjunction with  $\text{H}_2\text{O}_2$  at a controlled pH (2–6 range). The pH of the reaction medium was controlled by using appropriate buffer solutions.

Table 1  
Catalyst code and the metal content

Catalyst code	Metal	Inorganic support	Metal (wt%)
<b>Im1</b>	Cu	MCM-41	0.28
<b>Im2</b>	Co	MCM-41	0.64
<b>Im3</b>	Ni	MCM-41	0.58
<b>Im4</b>	Cu	Silica	0.40
<b>Im5</b>	Co	Silica	1.05
<b>Im6</b>	Ni	Silica	1.01

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