

## Oxidation of toluene and hydrogen peroxide catalyzed by Ni (II), Co (II), and Cu (II) Schiff base complexes

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**ABSTRACT:** There are only few reports on the selective oxidation of toluene is carried out at low temperatures using different oxidants like hydrogen peroxide, O<sub>2</sub> etc. Peroxides are very attractive, relatively cheap and waste-avoiding oxidants.

In this regard, a more environmentally benign, economically feasible and selective catalytic process is desirable. Transition metal complexes are effective and selective catalysts in a variety of organic reactions. Although these catalysts offered interesting results such as low influence of diffusion mechanisms on reaction performance, they become more useful if the separation process is tagged to recover them at the end of reaction especially for precious and strategic metal catalysts. Currently many transition metal ions complexes have been identified as homogeneous catalysts for various reactions, which showed high homogeneity, reproducibility, selectivity, and high activity to catalyze reactions under mild conditions.

Schiff base complexes of transition metal ions are efficient catalysts both in homogeneous and heterogeneous reactions. The liquid phase oxidation of toluene, in the presence of several Ni (II), Co (II) and Cu (II) Schiff base complexes using 30% aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant, was studied. Investigations have been carried out with a view to determining the most suitable reaction conditions with respect to operating variables including reaction temperature, batch time, concentrations of the substrate, catalyst, oxidant on the overall conversion and yield of products were studied. The selective oxidation of toluene with hydrogen peroxide will produce benzaldehyde, benzoic acid, benzyl alcohol.

Compared with the present synthetic method of benzaldehyde and benzyl alcohol by the chlorination of toluene followed by hydrolysis, which has been used in the world industry, the new method has the advantage of friendly environmental effects.

**Keyword:** Liquid phase; Toluene oxidation; Hydrogen peroxide; Schiff base complex

### I. INTRODUCTION

The catalytic oxidation of C-H bonds of hydrocarbons to oxygenated products under mild reaction condition is a major challenge in view of industrial aspects [1,2]. The oxygenated products are the required intermediates for many chemical feedstocks, agrochemicals, fragrances, pharmaceuticals and polymers. Moreover, the selectivities to the desired oxygenated products are always less. Thus, the selective catalytic oxidation of inactive hydrocarbons to industrially important oxygenated derivatives is still remains a major challenge [3-5]. Among various hydrocarbons, toluene is an important one that can be converted into oxidation products such as benzyl alcohol, benzaldehyde and benzoic acid. Among these products benzaldehyde is the most desirable product. However benzaldehyde is easily over oxidized to benzoic acid. Traditionally, benzaldehyde is produced by chain chlorination of toluene and saponification of the resulting dichloromethyl group to form the aldehyde, the product still contains the chlorinated impurities, does not meet food and drug grade specifications. The vapor phase oxidation of toluene with oxygen generally carried at high pressure (0.5-2.5 MPa) and seem too harsh for improving the selectivity of benzaldehyde [6]. There exists lot of difficulties in vapor phase oxidation of toluene such as control of over oxidation or combustion that leads to the formation of carboxylic acids, phenols or decomposition to carbon oxides (CO<sub>2</sub> and CO) and tar. [7]

Many Schiff base complexes of metal ions show excellent catalytic activity in oxidation of hydrocarbons like alkenes, cyclo-alkanes and alcohols. The Schiff base complexes of Ni (II), Co (II) and Cu (II) have been used successfully as catalysts in the oxidation of toluene in this study.

### II. EXPERIMENTAL

#### 2.1 Materials

All chemicals used in this work were reagent grade (AR/Aldrich), including salicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, methanol, ethanol, acetonitrile, toluene, hydrogen peroxide.

## 2.2 Characterization:

We have reported previously the synthesis and Characterization of these Schiff Base ligands and their complexes in details[8].

## 2.3 Synthesis of Schiff base ligands:

The Schiff bases have been prepared by the condensation reaction of a warm absolute ethanol or methanol solution of 4-nitroaniline (0.276 g; 2mmol) with salicylaldehyde(0.244g; 2mmol) ,5-bromosalicylaldehyde(0.402g,2mmol) and 5 chlorosalicylaldehyde (0.315g; 2mmol). The reaction mixture was refluxed and stirred until cooling, the product was filtered, washed with absolute ethanol and dried over desiccators and recrystallized in mixture of absolute ethanol and n-hexane. The color of 2-((4-nitro phenyl imino) methyl) phenol was orange and the colors of both, 4-bromo2-((4-nitro phenyl imino) methyl) phenol and 4-chloro 2-((4-nitro phenyl imino) methyl) phenol were yellow. The general structure the of Schiff base ligands used in this study is shown in Figure.1. Table.1.

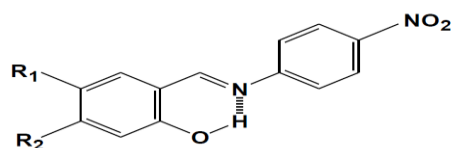


Figure 1. General Structure of the Schiff base ligands.

Ligand	Ligand's name	R1	R2
NMP	2-((4-nitro phenyl imino)methyl)phenol	H	H
BNMP	4-bromo2-((4-nitro phenyl) imino methyl)phenol	Br	H
CNMP	4-chloro 2-((4-nitro phenyl imino)methyl)phenol	Cl	H

Table.1: Schiff base ligands

## 2.4:for the Preparation of Schiff-Base complexes: General Procedure

Co (II), Cu (II), Ni (II) Schiff- Base complexes of this study were prepared as previously reported, in a similar way by a direct reaction of the corresponding metal acetate and ligand precursor (1:2 molar stoichiometric ratio). The solvents were selected so that the ligand precursors and metal acetates were fully dissolved but the complex precipitated out. All synthesized metal complexes were purified by washing with dry ethanol. The ligands (HNMP 0.0969g, 4mmol, BNMP0.1284g, 4mmol, CNMP0.1107g, 4mmol) were taken in ethanol and stirred gently for 30 minutes to give a homogeneous suspension. The ethanolic solution of Schiff base was magnetically stirred and refluxed with 2mmol metal acetate (1:2 metal-ligands) in ethanol for about 12 h. After refluxing, the volume of the solution was reduced to one third and the concentrate cooled at room temperature. The solid complex formed was filtered, washed with ethanol and dried in a desiccator. The structures of Schiff base complexes are shown in Fig.2.

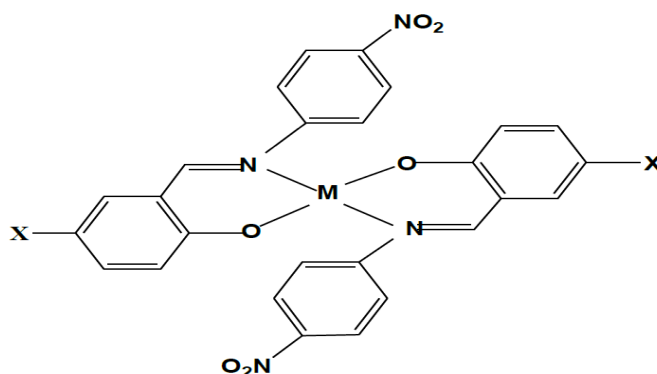


Fig.2. The structures of Schiff base complexes

**2.5:Procedure for the catalytic oxidation of toluene:** The toluene oxidation reactions were carried out in liquid phase at 70°C with addition of H<sub>2</sub>O<sub>2</sub>, in the presence of Co (II), Cu (II) and Ni (II) Schiff- Base complexes and ammonium acetate. The reactions were followed by GC and the addition of H<sub>2</sub>O<sub>2</sub> was stopped when two successive GC analyses showed no more conversion of the substrate. The procedure is described as follows:

In a typical reaction procedure, a mixture of 0.01 mol toluene (dissolved in 2ml acetonitrile) and 0.01 mmol catalysts was added into 50 ml double neck round bottom flask. Then aqueous hydrogen peroxide (30% w/w) was diluted in acetonitrile (2:5) and added to the reaction mixture in 37.5 l aliquots every 15 min. The oxidation was conducted with continuous stirring at 70°C. The progress of the reaction was monitored by TLC. After the reaction had been heated for 12 h, the mixtures were cooled, neutralized by 1 mol/L NaOH and separated. Benzoic acid (13.4 g) was obtained by filtering the water phase neutralized by 1 mol/L HCl. Toluene in the organic phase was recollected with the vacuum distillation at 40 mmHg and 33°C the benzaldehyde (10.2 g) at 15 mmHg and 69°C, and benzyl alcohol (10.2 g) at 15 mmHg and 94°C. The main oxidation products were benzaldehyde, benzyl alcohol and benzoic acid with the by-products p-cresol, o-cresol were identified by GC-MS analysis .

### III. RESULTS AND DISCUSSION

To evaluate the catalytic efficiency of various Co (II), Cu (II) and Ni (II) Schiff base complexes, the oxidation of toluene was studied with hydrogen peroxide using acetonitrile as solvent. It can be seen from Table 4. that the blank experiment no oxidation was observed under similar conditions in the absence of catalyst. Oxidation of toluene with hydrogen peroxide catalyzed by Schiff base complexes yields benzaldehyde, benzyl alcohol and benzoic acid. GC-MS analysis showed that the by-products of toluene oxidation were mostly p-cresol and o-cresol .The changes of product distribution of toluene oxidation with time are shown in Fig. 5. The plot shows that the amounts of benzaldehyde and benzyl alcohol increase rapidly in the initial 4.0 h. In the same period of time, the amount of benzoic acid increased slowly. With the further increase of time, the increase rate of benzaldehyde and benzyl alcohol slows, and then benzaldehyde and benzyl alcohol maintain the maximum yields, while benzoic acid increase significantly. Our studies found that in the presence of 0.01 mmol Schiff base complexes of  $[Cu(CNMP)_2]$  , 35% selectivity to benzaldehyde 77% conversion of toluene were obtained under the condition of 70°C. Compared with the present synthetic method of benzaldehyde and benzyl alcohol by the chlorination of toluene followed by hydrolysis, which have been used in the world industry, the new method has the advantage of friendly environmental effects. This process will be have great industrial prospects for the production of benzaldehyde because of its milder reaction condition, lower environmental pollution, and no more equipment investment compared to the conventional method of synthesizing benzaldehyde and benzyl alcohol.

#### 3.1 Effect of reaction temperature on toluene oxidation:

The effects of the reaction temperatures on the product selectivity, toluene conversion are shown in Table 2. The researchers found that the toluene oxidation with hydrogen peroxide catalyzed by Schiff base complexes is highly sensitive to the reaction temperature. The reaction could not take place when the temperature is below 25 °C. The reaction rate at 25 °C is so slow that there are no oxidation products before the reaction lasted 4h. But when the temperature is increased further to 70°C the selectivity of oxidation become difficult to control. The optimum temperature for toluene oxidation with hydrogen peroxide catalyzed by Schiff base complexes is 70°C.

Temperature(°C)	Conversion(%)
18	5/2
25	8/15
45	19/6
60	40
70	66

Table 2: Effect of reaction temperature on toluene oxidation:

#### 3.2 The effect of the amount of catalyst on toluene oxidation:

The effects of the amount of catalyst on the product selectivity and toluene conversion in the toluene oxidation are shown in Table 3. As can be seen from Table, the toluene conversion increases significantly with the increases of the amount of catalyst from 0.005 mmol to 0.02 and also these results show that the reaction time decreases with increase in catalyst concentration. But the toluene conversion decreases with the further increases of the amount of catalyst, the changes of the amount of catalyst are almost impervious to the products distributions. The optimum amount of catalyst is 0.01 mmol in this study.

Catalyst amount (mmol)	Selectivity (mol %)			Toluene conversion
	benzaldehyde	Benzyl alcohol	Benzoic acid	
0.005	17	13	10.24	21
0.01	34	24	31	64
0.02	35	24	37	65.5
No catalyst	0	0	0	0

Table 3. Toluene 0.01mol; the catalyst  $[Cu(CNMP)_2 \cdot H_2O]$ , 0.01mmol

### 3.3 Effect of concentration of toluene in the reaction mixture:

When the concentration of toluene was increased from 28 to 64(w/v% of the reaction mixture) in the liquid phase oxidation of toluene, the conversion of toluene and productivity with respect to all products was enhanced twofold. However, the selectivity toward benzaldehyde and benzyl alcohol, desired products in term of value addition, is almost the same, while yields with respective products are enhanced (Figure4). When the concentration of toluene was further increased to 80 w/v%, the overall conversion of toluene and productivity in terms of all product decreases significantly, because at this concentration, the catalyst mixture is not completely soluble in the reaction mixture.

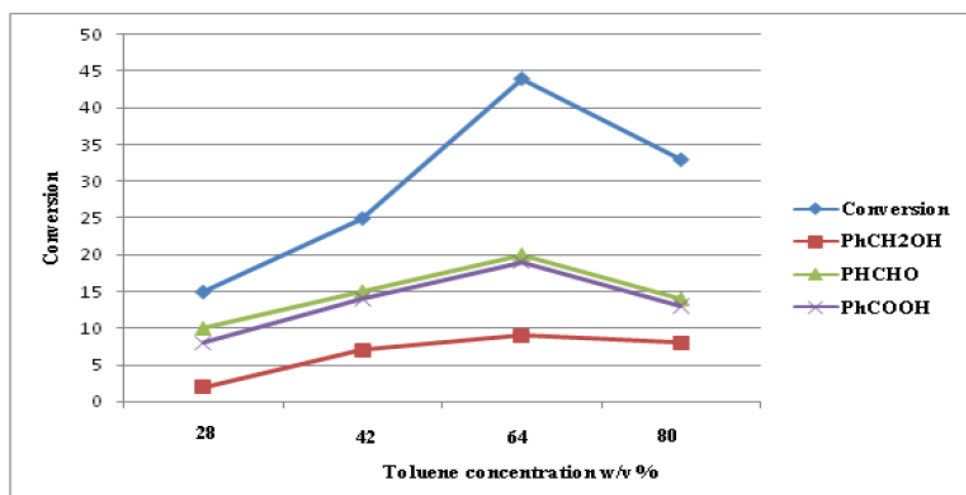


Figure4. Effect of concentration of toluene in the reaction mixture

### 3.4 Effect of reaction time on toluene oxidation:

The reaction profile during the oxidation of toluene with hydrogen peroxide over  $[Cu(CNMP)_2 \cdot H_2O]$  Schiff base catalyst has been studied. The variations of reaction products with time are measured and the results are shown in Fig5. The conversion rate of toluene in the first 3 h is low, it was observed from Figure3 that with an increase in period of reaction, the conversion of toluene also increased and the selectivity towards the three products is varied with reaction time. Initially the selectivity to benzyl alcohol and benzaldehyde is high. The formation of benzoic acid increased substantially at prolonged reaction and at the same time selectivity of benzyl alcohol is decreases. However, the variation in selectivity towards benzaldehyde is limited. These results suggest that further oxidation of alcohol is taking place with time to yield more benzoic acid, a stable oxidation product.

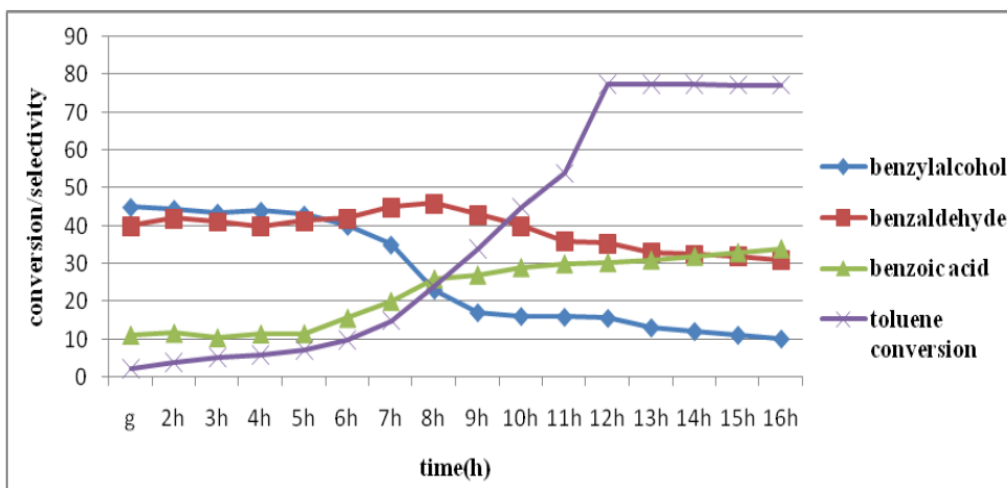


Fig5. The reaction profile during the oxidation of toluene with hydrogen peroxide over  $[\text{Cu}(\text{CNMP})_2 \text{H}_2\text{O}]$  Schiff base catalyst

### 3.5 Effect of using co-catalyst on toluene conversion and product selectivity:

The catalytic oxidation reaction of toluene carried out in the presence of Schiff base complexes as catalyst and acetonitrile as solvent and the effects of using ammonium acetate and sodium bromide as co-catalyst on toluene conversion were studied separately. The results showed that using 2mmol ammonium acetate as co-catalyst increases toluene conversion. Ammonium acetate is necessary for the required heterolytic cleavage of  $\text{H}_2\text{O}_2$ . It was also observed that benzyl nitrate is formed in the presence of ammonium acetate in the reaction mixture. By replacing sodium bromide with ammonium acetate as promoter, the overall conversion of toluene and yields of benzaldehyde are increased. On the other hand, the selectivity toward benzaldehyde is increased with increasing sodium bromide concentration.

### 3.6 Comparison of catalytic Activity of Ni (II), Co (II), and Cu (II) Schiff base complexes:

To evaluate the catalytic efficiency of various Ni (II), Co (II), Cu (II) Schiff base complexes, the oxidation of toluene was studied with hydrogen peroxide using different acetonitrile as solvent.

It can be seen from Table 4, that in blank experiment no oxidation was observed under similar conditions in the absence of catalyst. Among the 1-9 Schiff base catalyst, Cu (II) complexes gave the best conversion of 59-77.5%, and Co (II) complexes gave low conversion of 10-17% in the oxidation of toluene. GC-MS analyses of the post-reaction mixture of Cu (II), Ni (II) complexes showed that trace quantities of o-cresol and p-cresol were also detected. But there were no by products in the reaction mixture of Co (II) complexes.

Schiff base complexes	Conversion (%)	Selectivity%			
		Benzyl alcohol	benzaldehyde	Benzoic acid	by product
[Co(NMP) <sub>2</sub> ]	10.44	1.19	7.75	1.5	–
[Co(CNMP) <sub>2</sub> ]	17.44	2.27	11	4.17	–
[Co(BNMP) <sub>2</sub> ]	13.72	3.6	7.87	2.25	–
[Cu(NMP) <sub>2</sub> ]	59.22	17.5	28.9	10.82	2
[Cu(CNMP) <sub>2</sub> ]	77.5	18.9	35.45	19.15	4
[Cu(BNMP) <sub>2</sub> ]	65.45	19.56	32.5	11.09	2.3
[Ni(NMP) <sub>2</sub> ]	43.26	8.5	18.25	16	0.51
[Ni(CNMP) <sub>2</sub> ]	48.98	9.5	22	17	0.48
[Ni(BNMP) <sub>2</sub> ]	39.36	10	18.36	10.92	0.08
No catalyst	–	–	–	–	–

Table4. Reaction conditions: the substrate, 0.01mol; the catalyst, 0.01 mmol were dissolved in acetonitrile (2.0 ml) and stirred at 70 °C temperature. Aqueous hydrogen peroxide (30% w/w) was diluted in acetonitrile (2:5) and added to the reaction mixture in 37.5l aliquots every 15 min. Reaction time 12h.

#### IV. CONCLUSIONS

Benzaldehyde and benzyl alcohol were prepared with high selectivity and moderate toluene conversion by direct side chain oxidation of toluene with hydrogen peroxide catalyzed by the Schiff base complexes which has a greater catalytic performance than the other catalysts. The present catalytic system is environmentally benign, economical and non-corrosive.

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