



NOTE

Tetraazamacrocyclic Schiff Base Co(II) and Ni(II) Complexes as Catalysts for Hydroxylation of Phenol

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The catalytic activity of two tetraazamacrocyclic Schiff base complexes of Co(II) and Ni(II) with the composition CoL and NiL, respectively were studied by the liquid phase catalytic hydroxylation of phenol to catechol and hydroquinone using H₂O₂ as oxidant. In the presence of the catalysts, CoL and NiL, the 31.3 % phenol conversion was obtained with 52.6 % selectivity to benzenediol and the 33.6 % phenol conversion was obtained with 53.8 % selectivity to benzenediol under the optimum reaction conditions.

Key Words: Azamacrocyclic, Schiff base, Nickel(II) complex, Hydroxylation of phenol, Cobalt(II) complex, Catalyst.

Various metal complexes, which sometime show the high catalytic activities, have been used widely in homogeneous catalyzed reactions¹⁻⁵. Hydroxylation of phenol with 'green' oxidant H₂O₂ is one of the most promising industrial process. In previous works we showed that tetraazamacrocyclic Schiff base complexes are selective catalysts of the hydroxylation of phenol to benzenediol^{6,7}.

In this paper, the catalytic activities of the two tetraazamacrocyclic Schiff base complexes, CoL and NiL (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene-2ClO₄), for the hydroxylation of phenol reaction were studied.

All reagents were of AR grade and used without further purification. The CoL and NiL were synthesized according to the literatures^{8,9} and characterized by IR spectra and elemental analysis. The products of the catalytic phenol hydroxylation reaction were analyzed using an Agilent 1200 liquid chromatograph.

Catalytic activity studies: Experiments to study the catalytic activity of the Schiff base complexes were performed in a 50 mL with a temperature-controlled reactor and a backflow condenser and a magnetic stirrer. In a typical instance, 1.5 g of phenol and 20 mg of the catalyst were mixed in 22 mL of solvents. The reactor was heated to 50 °C with continuous stirring. 3 mL of hydrogen peroxide (30 %) was added dropwise to the refluxing mixture. After addition, the solution was refluxed for 5.0 h and the analysis was performed by Agilent 1200 LC with a UV-detector (277 nm).

Yields of the main reaction product catechol and hydroquinone (CAT and HQ) reported in following section were defined as $C_{\text{phen.}} (\text{mol } \%) = \{([\text{CAT}] + [\text{HQ}]) / [\text{ph}]\} \times 100$, where $C_{\text{phen.}}$ is the conversion of phenol (%), [ph] is the mol number of phenol in the material feeding and [CAT] and [HQ] are the mol numbers of catechol and hydroquinone produced.

Studies of the optimum reaction conditions: In order to achieve optimum reaction conditions for the hydroxylation of phenol, the following experimental parameters such as solvents, reaction temperature, reaction time, pH value and H₂O₂/phenol molar ratios seem to have influence on the catalytic activity of CoL and NiL.

Effect of reaction solvents on hydroxylation of phenol: Five different solvents (H₂O, C₂H₅OH, H₂O/C₂H₅OH (1:1), CH₃OH and DMF) were used to evaluate their influence on the catalytic performance of the complexes for the hydroxylation of phenol. The suitable reaction solvents were DMF for CoL and H₂O/C₂H₅OH (1:1) for NiL.

Effect of reaction temperature on hydroxylation of phenol: The hydroxylation of phenol was studied at different temperatures to determine the energy of activation in the temperature range of 30-80 °C. After many experiments, 50 °C was chosen as a suitable reaction temperature condition.

Effect of reaction time on hydroxylation of phenol: The influence of reaction time on the catalytic activity of the two tetraazamacrocyclic Schiff base complexes were studied at 50 °C. With the increase of reaction time, phenol conversion increased. After 5 h, the phenol conversion rises slowly, so the suitable reaction time was about 5 h.

Effect of pH value on hydroxylation of phenol: The acidity of reaction medium also had a remarkable influence on the phenol conversion. The experimental data indicated that the suitable reaction pH values were 5-6 for CoL and about 7 for NiL.

Effect of H₂O₂ concentration on hydroxylation of phenol: The effect of H₂O₂ concentration on hydroxylation of phenol was studied by varying the molar ratio of H₂O₂ to phenol from 1.0 to 4.0. The phenol hydroxylation was increased on increasing the molar ratio of H₂O₂ from 1.0 to 2.2 and the most appropriate molar ratio of H₂O₂ to phenol was at 2.2:1.

Catalysts for hydroxylation of phenol: The catalytic results of the hydroxylation of phenol reaction are listed in Table-1. It can be seen from Table-1 that CoL and NiL catalysts have high phenol conversion and certain catalytic selectivity for the catechol.

TABLE-1
CATALYTIC ACTIVITY IN THE
HYDROXYLATION OF PHENOL

Catalysts	Xphenol (%)	Selectivity (%)		CAT/HQ
		CAT	HQ	
CoL	31.3	32.0	20.6	1.55/1
NiL	33.6	34.7	19.1	1.82/1

Reaction conditions: reaction temperature 50 °C, H₂O₂/phenol (molar ratio) about 2.2; Reaction time 5 h, Solvent: DMF for CoL and water/ethanol (1:1), oxidant: H₂O₂; CAT = Catechol, HQ = Hydroquinone.

Conclusion

The experimental results of two tetraazamacrocyclic Schiff base complexes (CoL and NiL) catalysts revealed higher catalytic activity and certain catalytic selectivity for catechol in the reaction hydroxylation of phenol with H₂O₂ as oxidant, under mild reaction conditions.

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