Asian Journal of Chemistry; Vol. 24, No. 2 (2012), 935-936

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

NOTE

Catalytic Hydroxylation of Phenol by Co(II) and Ni(II) Complexes of An Tetraaza Macrocyclic Crown Ether

JIAN-HONG BI[1,*], ZI-LU YAO[2] and MAN CUI[3]

[1]Deparment of Chemistry and Chemical Engineering, Hefei Normal University, Hefei, P.R. China
[2]Department of Chemical Engineering and Technology, School of Materials Science and Engineering, Henan Polytechnic University, Jiao Zuo 454003, P.R. China
[3]Shuangdun Middle School, Changfeng County, Hefei 231131, P.R. China

*Corresponding author: E-mail: bi010101@126.com

(*Received*: 18 May 2011; *Accepted*: 24 October 2011) AJC-10564

The catalytic abilities of the two tetraaza macrocyclic crown ether complexes of Co(II) and Ni(II) with composition $CoL(ClO_4)_2$ and $NiL(ClO_4)_2$ in the hydroxylation of phenol with H_2O_2 was studied. When $CoL(ClO_4)_2$ was used as catalysts, 4.6 % phenol conversion was obtained with 87.5 % selectivity to diphenol. But when $NiL(ClO_4)_2$ was used as catalysts, 5.7 % phenol conversion was obtained with 80.8 % selectivity to diphenol under the optimum reaction conditions.

Key Words: Azamacrocyclic crown ether, Co(II), Ni(II), Complexes, Catalyst, Phenol, hydroxylation, Diphenol.

The benzenediol is a widely used industrial intermediates and could be obtained by hydroxylation of phenol in presence of catalyst. Due to its simple technology, low price and no pollution, hydrogen peroxide direct oxidation of phenol to manufacture hydroquinone (HQ) and catechol (CAT) is very competitive cleaning process[1-4]. There are few azamacrocyclic crown ether complexes reported as catalyst for this reaction until now[5,6].

In this paper, the catalytic abilities of the two tetraaza-macrocyclic crown ether complexes of Co(II) and Ni(II) with composition $CoL(ClO_4)_2$ and $NiL(ClO_4)_2$ (L = 5,5,7,12,12,14-hexamethyl -1,4,8,11-tetrazamacrocyclotetradecane) for the hydroxylation of phenol reaction were studied.

All reagents were of AR grade and used without further purification. The catalysts of $CoL(ClO_4)_2$ and $NiL(ClO_4)_2$ were synthesized according to the literature[7,8] 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: The catalytic activity study on the hydroxylation of phenol was carried out in a 50 mL flask fitted with a water-cooled condenser. In a typical reaction, phenol 0.2 g and the catalyst 20 mg were mixed in 30 mL of solvents (H_2O/C_2H_5OH = 1:1) and the reaction mixture was heated to 50 ºC with stirring. H_2O_2 (30 %, 6 mmol) was dripped to the reaction mixture slowly then reacted for 5 h. The products were analyzed using an Agilent 1200 liquid chromatograph with a ZORBAX Eclipse XDB-C18 column, 3:2 H_2O/CH_3OH as the mobile phase, and UV-VIS detection (λ = 277 nm). Yield of the reaction products (hydroquinone and catechol) reported in following section were defined as C_{phen} (mol %) = $\{([HQ] + [CAT]) / [ph]\} \times 100$, where [HQ] and [CAT] are the mol numbers of hydroquinone and catechol produced, C_{phen} is the conversion of phenol (%), [ph] is the mol number of phenol in the feed.

Reaction conditions: In order to achieve optimal reaction conditions for the hydroxylation, the following experimental parameters such as solvent type, reaction temperature, reaction time, pH value and H_2O_2/phenol molar ratio were studied in order to see their effect on the reaction product pattern.

Effect of reaction solvents: H_2O, ethanol, methanol, acetonitrile and their mixtures were used as solvents. Among them, test results displayed that water and ethanol (1:1) mixture is best solvent.

Effect of reaction temperature: The phenol conversion and product selectivity in reaction temperature range of 20-70 ºC were studied and 50 ºC was chosen as a suitable reaction temperature.

Effect of reaction time: The influence of reaction time on the catalytic activity of the two tetraaza macrocyclic crown ether complexes was studied at 50 ºC. With the increase of reaction time, phenol conversion increased. After 5 h, the reaction achieves steady-state, so the suitable reaction time is *ca.* 5 h.

Effect of reaction pH value: The acidity of reaction medium also has a remarkable influence on the phenol conversion. The experimental results showed that the suitable reaction pH is *ca.* 7.

Effect of H_2O_2/phenol molar ratio: The effect of the H_2O_2/phenol molar ratios on the phenol conversion and H_2O_2 conversion was studied. The experiment showed that the suitable H_2O_2/phenol molar ratio is *ca.* 3.

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 catalysts of $CoL(ClO_4)_2$ and $NiL(ClO_4)_2$ exhibited good catalytic selectivity for hydroquinone and catechol under the optimum reaction conditions.

TABLE-1
CATALYTIC ACTIVITY IN THE HYDROXYLATION OF PHENOL WITH H_2O_2

Catalysts	X_{phenol} (%)	Selectivity (%)		HQ/CAT
		HQ	CAT	
$CoL(ClO_4)_2$	4.6	63.2	24.3	2.6
$NiL(ClO_4)_2$	5.7	48.5	32.3	1.5

ACKNOWLEDGEMENTS

This work is financially supported by the National Natural Science Foundation of China (No. 20871039) and the Key Disciplines Foundation of Hefei Normal University.

REFERENCES

1. A. Dubey, V. Rives and S. Kannan, *J. Mol. Catal. A*, **181**, 151 (2002).
2. S. Lin, Y. Zhen, S.M. Wang and Y.M. Dai, *J. Mol. Catal. A*, **156**, 113 (2000).
3. J.H. Bi, L.T. Kong, Z.X. Huang, J.H. Liu, *Inorg. Chem.*, **47**, 4564 (2008).
4. H.S. Abbo, J.J. Salam, T.R. Prasad and S. Chand, *J. Mol. Catal. A*, **225**, 225 (2005).
5. J.H. Bi, M. Li and Y. Chen, *Asian J Chem.*, **22**, 7389 (2010).
6. J.H. Bi, B.Z. Li, F.Y. Yao and N.L. Hu, *Asian J. Chem.*, **22**, 8199 (2010).
7. J.H. Bi, *Acta Cryst.*, **E65**, m633 (2009).
8. J.H. Bi, Y.Y. Cao and M. Cui, *Asian J. Chem.*, **22**, 8143 (2010).