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NOTE

Oxidation of Phenol by Two Tetraazamacrocyclic Cu(II) Complexes Catalysts

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The catalytic oxidation of phenol to hydroquinone and catechol was performed in the presence of the two tetraazamacrocyclic copper(II) complexes of $CuL_1(ClO_4)_2$ and $CuL_2(ClO_4)_2$ using H_2O_2 as oxidant and DMF as solvent. When the $CuL_1(ClO_4)_2$ and $CuL_2(ClO_4)_2$ were used as catalysts, 31.4 % phenol conversion was obtained with 48.1 % selectivity to diphenol and 29.9 % phenol conversion was obtained with 43.4 % selectivity to diphenol in the optimal reaction conditions.

Key Words: Tetraazamacrocycle, Catalyst, Copper(II) complexes, Phenol, Dihydroxybenzene.

Phenol is considered a cancer-causing pollutant. It is one of current hotspots that phenol transformed into industrial raw material benzenediol. The benzenediol, especially the hydroquinone (HQ) and catechol (CAT), are widely used in photographic chemicals, pharmaceutical, polymerization inhibitors, antioxidants and flavouring industries[1-5]. Direct oxidation of phenol with clean oxidant H_2O_2 has known to be less of an environmental pollutant[6,7] in the present of catalyst. However, few examples were reported that the tetraaza macrocyclic complexes as the catalysts for this reaction[8,9].

In this paper, the catalytic activities of the two tetraaza macrocyclic complexes $CuL_1(ClO_4)_2$ (L_1 = 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetra- azamacrocyclic-4,11-diene) and $CuL_2(ClO_4)_2$ (L_2 = 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetrazamacrocyclotetradecane) in the oxidation of phenol with H_2O_2 and the reaction parameters were evaluated.

All reagents were of AR grade and used without further purification. The $CuL_1(ClO_4)_2$ and $CuL_2(ClO_4)_2$ were synthesized according to the literature[10,11]. The products of the catalytic phenol oxidation reaction were detected using an Agilent 1200 liquid chromatograph with a ZORBAX Eclipse XDB-C18 4.6 × 150 mm column, methanol and water (V_{CH_3OH}/V_{H_2O} = 2:3) as the mobile phase, resorcin as internal standard and UV-VIS detection (λ = 277 nm).

Oxidation of phenol by H_2O_2 using the catalysts: The catalytic characteristic study on the oxidation of phenol was performed in a 50 mL flask fitted with a water-cooled condenser. In a typical run, phenol 1 g and the catalyst (10 mg) were mixed in 20 mL of DMF and the reaction mixture was heated to 50 ºC with magnetic stirring. An aqueous solution of 30 % H_2O_2 (3 mL) was added to the reaction mixture slowly and reacted at 50 ºC for 5 h. The products were detected using an Agilent 1200 liquid chromatograph. Yields of the main reaction product (HQ and CAT) reported in following section were defined as C_{phen} (mol %) = {([HQ] + [CAT]) / [ph]} × 100, where C_{phen} is the conversion of phenol (%), [ph] is the mol number of phenol in the feed and [HQ], [CAT] are the mol numbers of hydroquinone and catechol produced.

Study on the reaction conditions of oxidation of phenol: In order to optimize the reaction conditions, the following experimental parameters such as the effect of reaction temperature, reaction time, catalyst mass, pH value and molar ratio of reactants were studied for their effect on the reaction product pattern.

Effect of reaction temperature: The phenol conversion and product selectivity in reaction temperature range of 20-70 ºC were studied. Based on the results obtained, 50 ºC was determined as the optimal reaction temperature for phenol oxidation with the two tetraazamacrocyclic complex catalysts.

Effect of reaction time: The influence of reaction time on the catalytic activity of the two tetraazamacrocyclic copper(II) complexes catalysts was studied at 50 ºC. With the increase of reaction time, phenol conversion increased. After 5 h, although phenol conversion still increased, but the reaction products achieved steady-state, so the optimal reaction time is *ca.* 5 h.

Effect of pH value: The acidity of reaction medium also has a remarkable influence on the phenol oxidation reaction. The experimental results indicated that the optimal reaction pH is *ca.* 4.6.

Effect of molar ratio of reactants: The effect of the H_2O_2/phenol molar ratios on the phenol oxidation reaction was studied. The experimental data indicated that the optimal H_2O_2/phenol molar ratio is *ca.* 3.

Catalysts for oxidation of phenol: The catalytic results of the oxidation of phenol reaction are listed in Table-1.

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

Catalysts	Xphenol (%)	Selectivity (%)		HQ/CAT
		HQ	CAT	
$CuL_1(ClO_4)_2$	31.4	29.6	18.5	1.60
$CuL_2(ClO_4)_2$	29.9	25.6	17.8	1.44

Reaction conditions: Reaction temperature 50 ºC, Reaction time 5 h; H_2O_2/phenol (molar ratio) is about 3, pH is about 4.6.
HQ = Hydroquinone; CAT = Catechol.

It can be seen from Table-1 that $CuL_1(ClO_4)_2$ and $CuL_2(ClO_4)_2$ catalysts have high phenol conversion and certain catalyzed selectivity for the phenol oxidation. This phenomenon indicates that the tetraazamacrocyclic complexes would be potential catalysts for the phenol oxidation reaction.

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