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Catalytic Oxidation of 2-Mercaptoethanol by Cobalt(II)phthalocyanines Bearing Chalcone with Furan and Thiophene

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Abstract

Cobalt (II) phthalocyanines carrying on the four of the peripheral positions furan and thiophene as chalcones were sythesized. THF is used to investigate the catalytic oxidation of 2-mercaptoethanol. The synthesized phthalocyanines show catalytic activity on the oxidation of 2-mercaptoethanol. Cobalt (II) phthalocyanine derived by chalcone with furan has given catalytic specifications such as turnover number TON as 16.6, initial reaction rate as 0.293 µmol/sec and the oxygen consumption as 10.06 µmol/min. The other cobalt (II) phthalocyanine derived by chalcone with thiophene has given catalytic specifications such as turnover number TON as 15.9, initial reaction rate as 0.213 µmol/sec and the oxygen consumption as 9.88 µmol/min. So chalcone derived phthalocyanines can be used as catalyst is oxidation of mercaptan by air.

Keywords: Catalysis, 2-mercaptoethanol, oxidation, phthalocyanine

1. INTRODUCTION

Alkyl thiol compunds, known as mercaptans, are highly polluting compounds. The removal of thiol compounds is not only important in preventing environmental pollution. Furthermore, mercaptan compound poisons the catalysts those are added into the the petroleum products such as petrol and diesel for enhancing the performance. So the mercaptan oxidation process is used for the removal of thiols. The mercaptan oxidation is carried out by oxygen in the air and catalysts. This aerobic oxidation process of thiols is studied by using both homogeneous and heterogeneous catalysts [1-7].
Phthalocynines (Pcs) have flexibility in structure. Adding some organic groups to peripheral or non peripheral positions and also changing the metal ion in the center of Pcs empowers the new properties. Metallophthalocyanines have active center like natural metalloenzymes. This similarity give the enzyme like activities to the phthalocyanines. Cobalt (II) ion in the center of phthalocyanine is giving the catalytic property to Pc. Cobalt (II) ion in the center of two dimensional planar molecule can interact with both mercaptan and dissolved oxygen by the opposite sides but on the same line. The catalytic reaction occurs by this interaction [8-17]. Chalcone is an aromatic ketone that forms the center of many biological compounds. The aldol condensation reaction can be used to synthesis chalcones. This reaction is carried out between benzaldehyde and acetophenon while sodium hydroxide as catalyst. Chalcones are also intermediate step in the biosynthesis of flavonoids having biological activities. The electron transfer will take place between conjugated chalcone structures and phthalocyanine [18].
We have studied before catalytic oxidation of 2-mercaptoethanol by water soluble porphyrazine complex and made this catalyst as heterogeneous by immobilizing on a polyester woven fabric as dye [8,9]. In this study the chalcone derived cobalt (II) phthalocyanines are used as catalyst for the oxidation of 2-mercaptoethanol. In our previous published research paper acetophenon derived chalcone group is used for derivatizing the phthalocyanine and used as catalyst for oxidation of 2-mercaptoethanol. In this study two chalcone groups these are 2-acetylfuran and

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2-acetylthiophene are used to obtain chalcone by the reaction with 4-hydroxybenzaldehyde and then used in the synthesis of chalcone substituted metallophthalocyanine.

2. GENERAL REQUIREMENTS

2.1. General

The glassware used in this study is heated at 150 °C for 1h and cooled under inert nitrogen atmosphere then used in all experimental step. The fine chemicals used during the experimental section provided from commercial suppliers. A double walled glass reactor created and used for investigation of catalytic reaction. Dissolved oxygen in the reactor is measured by CYBERSCAN D300 oxygenmeter.

2.2. Synthesis of Catalysts

Figure 1 shows the synthetic route for Co(II)phthalocyanines, catalysts. The synthetic procedures are used as written in the literature and obtained compunds show same spectroscopic results [19-21].

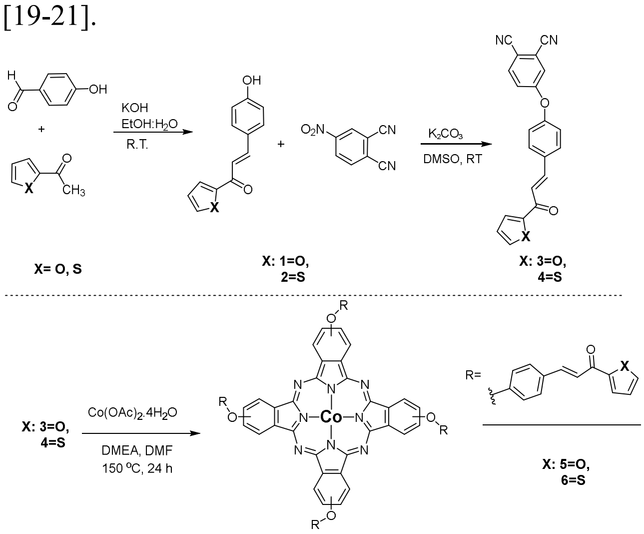

Figure 1. The synthetic route for Co(II)phthalocyanines, 5-6.

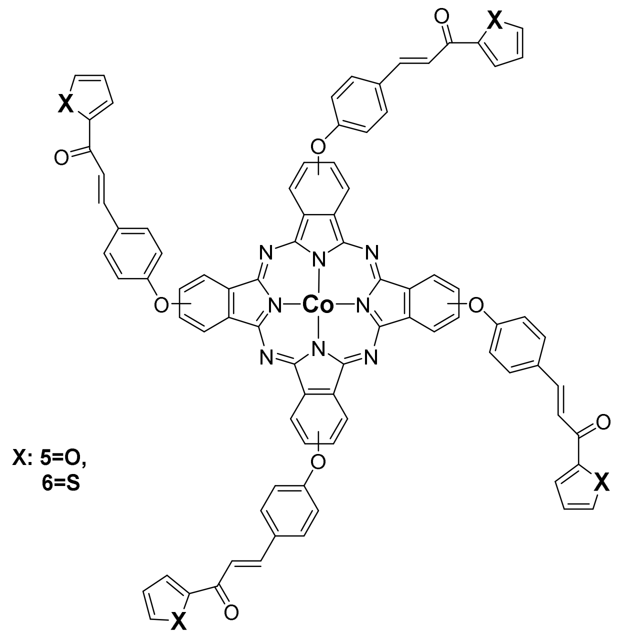

Figure 2. Co(II)Phthalocyanines

2.3. Catalytic oxidation of 2-mercaptoethanol

Catalytic oxidation of 2-mercaptoethanol was followed by measuring dissolved oxygen in the reactor in that the catalytic process was carried out by CyberScan DO 300. Both Co(II)phthalocyanines, **1** and **2**, were wieghed 0.152 μmoL in 50 mL THF. Air is passed through into the solution by bubbling in the reactor in order to saturation of oxygen in the solution. 1 mL of 0.25 wt% aqueous sodium hydroxide solution was joined into the reaction vessel in order to make alkaline the solution. 7,3 μL (1.52 mmol) 2-mercaptoethanol was added by micropipette. The molar ratio of catalyst, Co(II)phthalocyanine, and substrate, 2-mercaptoethanol, was 1:10000. This ratio is very good ratio to measure catalytic effect. At the same time, recording of the measured dissolved oxygen was started. Because the oxygen comsuption was started by catalytic oxidation of 2-mercaptoethanol. Then oxygen consumption was calculated depending on time.
The mercaptan/molecular oxygen ratio is 4/1 in all mercaptan oxidation method [2].

$$4RSH + O_2 \rightarrow 2RS\text{-}SR + 2H_2O \qquad (1)$$

The rate of mercaptan oxidation was calculated by the decreasing of dissolved oxygen.

3. RESULTS AND DISCUSSION

The catalytic oxidation of 2-mercaptoethanol by Co(II)phthalocyanines is well known in the literature. The Co(II)phthalocyanines those are derived by chalcone and by thio chalcone group are synthesized by our group. Both of the metallophthalocyanines show

non-aggregation behaviour. This is very important for catalytic activity on oxidation of mercaptans. The opposite sides of metal center of Co(II)phthalocyanines can coordinate with substrate and oxygen. Because thio alcohol RSH is dissociated as RS^- anion and H^+ in alcaline solution made by sodium hydroxide addition. The formed RS^- anion will coordinate to the metal center and O_2 on the other side of the metal center of Co(II)Pc. One electron is transferred from the thiolate to oxygen through the mmetal center of Co(II)Pc and so disulfied occures. The catalytic reaction between 2-mercaptoethanol and oxygen is seen in equation (1). The ratio of thiol/catalyst is 10000 as catalytic concentration. After a small amount of NaOH solution was added into the mercaptan (RSH) solution, thiolate (RS^-) anion will be produced and then Co(II)Pc will start to catalyse the oxidation of 2-mercaptoethanol
Both cobalt (II) phthalocyanines show very close results. Because both chalcones have very similar structure. The only difference between the structures are O and S atoms. The very big phthalocyanine skeleton and chalcone compunds have conjugated structures. So the effect of O and S atos in the furan ring will be reduced.
Figure 3 shows the oxygen consumption in the reaction of catalytic oxidation of 2-mercaptoethanol by Co(II)Pc substituted by chalcone with furan as catalyst in THF.
The value that makes the first derivative of the equation zero gives the initial reaction rate, as 0.293 µmol/sec. Turnover number, TON, (mol oxygen per mol phthalocyanine), is calculated as 16.6. The oxygen consumption was calculated as 10.06 µmol/min.
Figure 4 shows the oxygen consumption in the reaction of catalytic oxidation of 2-mercaptoethanol by Co(II)Pc substituted by cahlacone with thiophene as catalyst in THF.

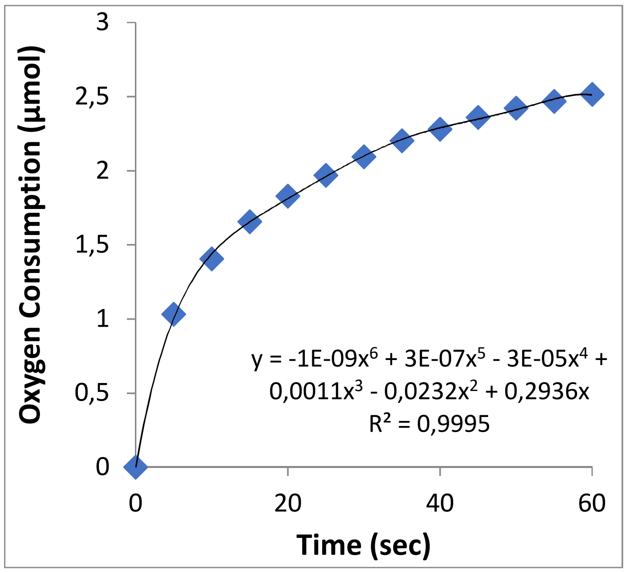

Figure 3. Oxygen consumption in the reaction of catalytic oxidation of 2-mercaptoethanol by Co(II)Pc substituted by chalcone with furan as catalyst in THF.

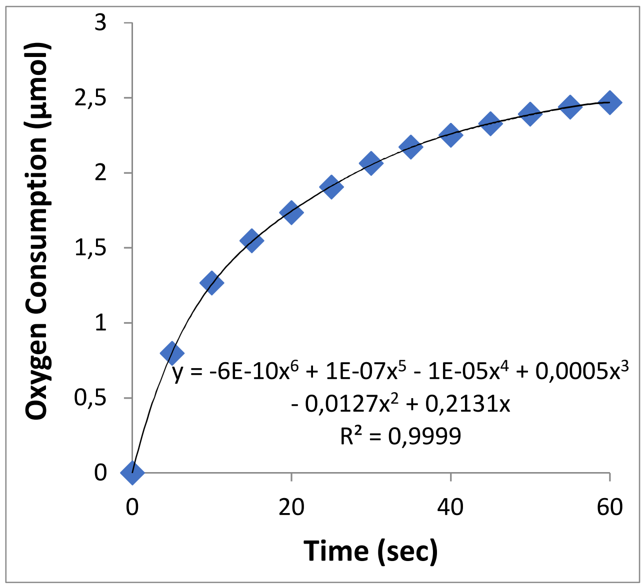

Figure 4. Oxygen consumption in the reaction of catalytic oxidation of 2-mercaptoethanol by Co(II)Pc substituted by chalcone with thiophene as catalyst in THF.

The value that makes the first derivative of the equation zero gives the initial reaction rate, as 0.213 µmol/sec. Turnover number, TON, (mol oxygen per mol phthalocyanine), is calculated as 15.9. The oxygen consumption was calculated as 9.88 µmol/min.

4. CONCLUSION

In conclusion, both Co(II) phthalocyanines which are substituted with chalcone with furan and thiophene have been synthesized and characterized. These phthalocyanines were synthesized by a synthetic route shown in figure 1. Both cobalt (II) phthalocyanines are nonaggregable and soluble is common organic solvents. THF is used to investigate the catalytic oxidation of 2-mercaptoethanol. The catalytic oxidation of 2-mercaptoethanol by cobalt (II) phthalocyanines is very much studied reaction. So the synthesized phthalocyanines show catalytic activity on the oxidation of 2-mercaptoethanol.

Cobalt (II) phthalocyanine derived by chalcone with furan has given catalytic specifications such as turnover number TON as 16.6, initial reaction rate as 0.293 μmol/sec and the oxygen consumption as 10.06 μmol/min.

The other cobalt (II) phthalocyanine derived by chalcone with thiophene has given catalytic specifications such as turnover number, TON, as 15.9, initial reaction rate as 0.213 μmol/sec and the oxygen consumption as 9.88 μmol/min.

So chalcone derived phthalocyanines can be used as catalyst is oxidation of mercaptan by air.

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