Synthesis, Characterization and Catalytic Activity of CuO/ZnO on Phenol Oxidation

Nuni Widiarti³, Sri Wahyuni³, S Barokah³

Abstract

Oxidation of phenol with H₂O₂ as oxidant by use of CuO/ZnO catalysts has been studied. ZnO was synthesized with coprecipitation method, was continued by the process of the impregnation ZnO with the precursor Cu(NO₃)₂·3H₂O produced the catalyst of CuO/ZnO. Synthesis results of ZnO and CuO/ZnO catalysts were characterized by using XRD,DR-UV. The catalytic activity him was tested in an oxidation reaction of phenol. Results of the characterisation with X-ray diffraction showed that the catalyst ZnO resulted from the synthesis has a wurzite structure and all the catalysts synthesized have nano-sized structure. The characterisation with DR-UV showed that the energy gap decreased with increasing concentration of Cu that was added in ZnO. The optimum conditions for the oxidation of phenol with 50% CuO/ZnO and oxidant H₂O₂ in the time variation 1 to 5 hour was observed when the reaction lasted 2 hours with methanol solvent. Phenol was degraded by 0.6903 mmol, and 6.48% conversion and selectivity to hydroquinone 44.49% was obtained. Whereas to the catalyst of XCuO/ZnO the conversion phenol increased with the rise loading CuO 10% as far as 50%, and descended again in CuO 70%.

Keywords: Oxidation phenol, ZnO, CuO/ZnO, methanol.

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Introduction

Hydroquinone is a useful compound for industrial world such as: photography, X-ray in hospitals, antioxidant in rubber industries, monomer stabilizer, paint stabilizer, fuel, organic synthesis, and as perfume material. Hydroquinone synthesis is generally produced through phenol oxidation reaction (Endahroyani, 2009).

A method that is being developed for phenol oxidation is photocatalytic. Photocatalytic oxidation is a phenol oxidation method with the existence of oxidizing and catalyst supported with UV exposure. Zhang and Lian (2009) have conducted phenol oxidation using TiO₂ nano crystalline catalyst, which produced selectivity toward hydroquinone as much as 50%. The general oxidizing material often used in photocatalytic reaction is hydrogen peroxide (H₂O₂). According to Clerici et al., (2001), H₂O₂ is stable, having higher active oxygen, so that it is suitable to be used as an oxidizing in phenol oxidation research.

Photocatalytic phenol Oxidation using CuO/ZnO aims to oxidation phenol into hydroquinone and catechol by distributing active metals on semiconductor’s surface with the most efficient ways so that it can be obtained a large surface and maximum activities. As an active catalyst, ZnO has quite high activities. from several research that have been reported before, Cu, both as metal ion and metal oxide, has an important role in phenol oxidation combined with ZnO to raise catalytic activities of ZnO.

Research Methods

Equipment that was used in this research including UV light, instrument X-Ray Diffraction (XRD), DR-UV and Gas Chromatography. Materials that were needed in this research were Zinc (II) Acetate dihydrate, Copper (II) Nitrate, Oxalic Acid, aquadest, NaOH, Methanol, acetone, phenol, hydroquinone, nitro benzene and hydrogen peroxide with grade for analyst made by Merck.

ZnO Catalyst was first synthesized according to coprecipitation method by Muslimin (2009) and Mukhtar et al., (2012). The mixing process was done by adding oxalic acid slowly into zinc solution and being stirred with magnetic stirrer. This mixture was stirred for 12 hours. The deposite produced was then filtered and cleaned with water and acetone. The solid material was then dried on the temperature of 110- °C for about 30 minutes and calcinated on the temperature of 450 °C for about 5 hours. While CuO/ZnO synthesis process was done through impregnation method, that was putting ZnO solid into 25 mL Cu(NO₃)₂·3H₂O solution. The produced solid was
then characterized using XRD and DR-UV. Then it was conducted a photocatalytic activities test of CuO/ZnO catalyst toward phenol oxidation reaction with reaction time and catalyst variation.

**Results and Discussions**

ZnO was synthesized according to any procedures conducted by Muslimin (2009) and Mukhtar et al., (2012) using coprecipitate method. This research used an organic acid, it was oxalate acid as a precipator agent. The benefit of using oxalic acid as a precipator agent was the result of the precipitation was so pure and there was no poisonous compound on the semiconductor while calcining (Muslimin, 2009). On the calcining process, the oxalate acid was decomposed into H$_2$O and CO$_2$ so that there was no pollutant left in ZnO and CuO/ZnO.

The reaction in the production of oxalate mineral (Muslimin, 2009) was:

$$\text{Zn(CH}_2\text{COO)}_2 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{ZnC}_2\text{O}_4 + 2\text{CH}_3\text{COOH}$$

$$\text{Zn(CH}_2\text{COO)}_2 + \text{Cu(NO)}_3\text{H} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Zn(C}_2\text{O}_4\text{)}_2\text{Cu} + 2\text{CH}_3\text{COOH} + 2\text{HNO}_3$$

The CuO/ZnO solid was obtained through impregnation method from Cu(NO)$_3$H$_2$O solution as a precursor of CuO. The oxide forming (calcination 450 °C, 3 hours).

$$\text{ZnC}_2\text{O}_4 \rightarrow \text{ZnO} + \text{CO}_2$$

$$\text{Zn(C}_2\text{O}_4\text{)}_2\text{Cu} \rightarrow \text{CuO/ZnO} + \text{CO}_2$$

The blueish-white solid obtained from the impregnation method was getting concentrated as long as the increasing amount of loading copper. The solid calcination was produced on the temperature of 450 °C for about 3 hours to remove organic template, decomposition of Cu(NO)$_3$H$_2$O became CuO, and to build strong structure on the catalyst (Widiarti, 2011). The CuO/ZnO solidform from the result of calcination was black, this colour was dominantly from the colour of copper oxide.

The characterization of XRD was used to look for information about crystallinity. Tops of X-ray diffraction were recorded with the range about 20=30–70 °C. Patterns of X-ray diffraction for CuO/ZnO (10, 30, 50, and 70%) had similar diffraction patterns, as shown on the Figure 1.

**Figure 1.** Diffractogram X-ray 10% CuO/ZnO, 30% CuO/ZnO, 50% CuO/ZnO, and 70% CuO/ZnO.

The diffraction patterns of CuO/ZnO as the result of synthesis process had the highest peak about 20= 31.18; 34.45; 36.32; ±76.12; and 56.63. in line with XCuO/ZnO, ZnO had also single diffraction peak in the area of 20=31.57 (Yulianti et al., 2011) which indicate that symmetry form of ZnO was wurtzite structure of ZnO crystal on hexagonal phase (JCPDS no. 80-0075).

The top of the diffraction of crystalline CuO as the result of precursor calcination Cu(NO)$_3$H$_2$O in the temperature of 550 °C for 5 hours was around 20=35.4 and 38.6 with Miller index (hkl) 111 (Widiarti, 2011). The top of the diffraction of CuO was similarly obtained from the result of precursor calcination CuSO$_4$.5H$_2$O (Mukhtar et al., 2012) and also precursor Cu(CH$_3$COO)$_2$ (Saravanan et al., 2013). While the X-ray diffraction pattern of XCuO/ZnO in Figure 1 showed combined diffraction pattern between CuO and ZnO. The top of the catalyst diffraction of crystalline CuO was shown by the top of diffraction around 20= 35.4 and 38.6 and was visible in 10% CuO/ZnO. The amount of CuO in ZnO did not influence the structure of ZnO, but it influenced crystallinity of ZnO that was getting reduced significantly as long as the increasing amount of CuO (Widiarti, 2011).

The characterization of DR-UV was conducted to search for gap energy on the synthesized semiconductor. The value of gap energy on the semiconductor was very important since it would influence the performance of semiconductor in channelling electron and hole. On the synthesized semiconductors of ZnO and XCuO/ZnO (10, 30, 50 and 70%) it was obtained the value of gap energy as shown in the Table 1.

**Table 1.** Gap energy of ZnO, XCuO/ZnO (10, 30, 50 and 70%) DR-UV characterization results
It was concluded from this research that the result of band gap was getting reduced. This was in line with the Mukhtar et al., (2012) who stated that the band gap would be continuously reduced along with the increasing amount of additional Cu concentration.

All the ZnO and XCuO/ZnO catalyst (10%, 30%, 50% and 70%) was then examined on its catalytic activities in phenol oxidation reaction using\textit{H}_2\textit{O}_2 oxidant. The result product from the phenol oxidation reaction was then analysed using Gas Chromatography by comparing chromatogram as the result of the reaction with hydroquinone standard chromatogram.

Based on the result of chromatogram with the time variation of phenol oxidation reaction for 1,2,3,4, and 5 hours, the most optimum one was 2 hour-time reaction. Table 2 showed catalytic activities 50% of CuO/ZnO on the time reaction of 1-5 hour-reaction. The phenol oxidation reaction with the catalyst of 50% of CuO/ZnO started to produce reaction products (hydroquinone and catechol) after 2-hour-reaction.

### Table 2. Results catalytic oxidation reaction of phenol with 50% CuO/ZnO, oxidant \textit{H}_2\textit{O}_2 to variation of reaction time using methanol solvent

<table>
<thead>
<tr>
<th>Reaction time (hours)</th>
<th>First mol phenol (10^{-2})</th>
<th>End mol phenol (10^{-4})</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.063</td>
<td>6.0321</td>
<td>6.0321</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.064</td>
<td>6.9036</td>
<td>6.4883</td>
<td>44.49</td>
</tr>
<tr>
<td>3</td>
<td>1.063</td>
<td>6.4038</td>
<td>6.0242</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>1.064</td>
<td>6.8443</td>
<td>6.4323</td>
<td>5.14</td>
</tr>
<tr>
<td>5</td>
<td>1.064</td>
<td>6.7818</td>
<td>6.3738</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 2 showed the amount of degraded phenol were increased in 2-hour-reaction, it was in line with phenol conversion and its selectivity, that was 6.4883% and 44.49%, but the increased amount of degraded phenol and its conversions after 2-hour reaction was insignificant. This showed that the phenol oxidation reaction was effective for 2 hours. However, the longer the time reaction, the phenol conversion would be decreased, followed by reduced selectivity toward hydroquinone. This was because the existence of side products marked with many other chromatogram peaks that appeared. This result was strengthen with Widiarti’s research (2011), showing the increasing number of time reaction would reduce its catalytic activities.

The phenol oxidation reaction was also conducted on XCuO/ZnO (10%, 30%, 50% and 70%) catalyst. There was no hydroquinone on the XCuO/ZnO catalyst but only succeed to degraded phenol. Non-existence of reaction products on XCuO/ZnO was possibly because the weak adsorption ability of the \textit{H}_2\textit{O}_2 oxidant on the catalyst’s surface. The \textit{H}_2\textit{O}_2 oxidant was less adsorbed on the catalyst’s surface and active species of Cu and Zn which played a role in phenol conversion, forming hydroquinone and catechol products. The adsorption of \textit{H}_2\textit{O}_2 oxidant on the catalyst’s surface was a key to produce some products in phenol oxidation reaction (Wilkenhoner et al., 2001).

This was possibly because sample storage time before being analysed with the gas chromatography was too long, so that the phenol was then oxidation, where the benzoquinone and catechol changed into Tar, marked with the dark chocolate of the solution, and the hydroquinone changed into Benzoquinone. The phenol conversion as the result of phenol oxidation reaction with \textit{H}_2\textit{O}_2 oxidant could be seen on Table 3 and Figure 2.

### Table 3. Results of the oxidation reaction of phenol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial of Phenol (10^{-2})</th>
<th>Final of Phenol (10^{-4})</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>1.062</td>
<td>5.079</td>
<td>53.2877</td>
</tr>
<tr>
<td>CuO</td>
<td>1.064</td>
<td>5.154</td>
<td>84.3882</td>
</tr>
<tr>
<td>10% CuO/ZnO</td>
<td>1.063</td>
<td>5.432</td>
<td>34.4686</td>
</tr>
<tr>
<td>30% CuO/ZnO</td>
<td>1.064</td>
<td>5.675</td>
<td>48.2036</td>
</tr>
<tr>
<td>50% CuO/ZnO</td>
<td>1.064</td>
<td>5.316</td>
<td>68.4466</td>
</tr>
<tr>
<td>70% CuO/ZnO</td>
<td>1.064</td>
<td>5.028</td>
<td>43.0007</td>
</tr>
</tbody>
</table>
Table 3 showed that the phenol conversion was sharply increased on ZnO catalyst followed by CuO, but it was decreased for the XCuO/ZnO catalyst. This showed that CuO itself was effective enough to degraded phenol rather than CuO impregnated to ZnO with the ratio of XCuO/ZnO (10, 30, 50 and 70 %).

From the Figure 2, it was concluded that on XCuO/ZnO catalyst, the phenol conversion was increased along with increasing amount of CuO loading from 10% to 50% and was decreased back into CuO 70%. However, the combination of CuO/ZnO exactly reduced catalytic activities of CuO and ZnO. This reduced activities was caused by blockade of ZnO pores by metal oxide of CuO, so that the active side of the catalyst was covered and then obstructed oxidant adsorption of H2O2 into the active side of the catalyst. This was strengthen by Widiarti (2011), showing that the increasing amount of CuO in TS-1 for the reaction of benzene hydroxylate would create conversion and the selectivities toward the phenol would be reduced.

Conclusions

By examining the result of phenol oxidation reaction using ZnO, CuO, and XCuO/ZnO catalyst with the oxidant H2O2 catalyst, it was showed that the CuO catalyst had higher catalyst catalytic activities than ZnO and XCuO/ZnO.

References