Preparation of zinc oxide catalyst with activated carbon support for ozone decomposition

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Abstract. Investigation of catalyst for ozone decomposition was carried out by using zinc oxide (ZnO) catalyst and granular activated carbon (GAC) support. Ozone needs to be decomposed because it is harmful to human and can lead to death. Before GAC was used as a support, GAC was pre-treated using chloride acid (HCl) and sodium hydroxide (NaOH) to remove impurities. ZnO was impregnated onto the surface of GAC by using zinc carbonate (ZnCO₃) solution as precursor and then calcined at 300 °C to decompose carbon dioxide (CO₂). Size of GAC and loading percentage of ZnO were varied to get the highest catalytic activity. Size of GAC was varied between 18 – 100 mesh and loading percentage was between 0 – 2% w. The morphology, composition, and crystal phase were characterized by BET, SEM-EDX, and XRD method. From XRD method, crystal phase of catalyst was changed from ZnCO₃ structure to ZnO when calcined with exact temperature. Ozone decomposition was performed at room temperature and atmospheric pressure using fixed bed reactor. ZnO/GAC with smallest size (60 – 100 mesh) and highest loading percentage (2% w) showed the highest activity which the conversion reached 100% for 30 minutes. ZnO/GAC with smallest size and highest loading percentage had the largest surface area and the most active sites to decompose ozone.

1. Introduction

Need of catalyst for ozone decomposition is continued to increase with the excessive use of ozone in many industries. Ozone is a powerful oxidant and can be used as a disinfectant to remove unwanted chemical compound, bacteria, and even virus [1]. However, some industries do not have ozone destructor unit and the excess of ozone is released to the air, which has reached 2000 ppm. This level exceeds the allowed threshold which is 0.1 ppm for 8 hours [2]. This excess of ozone is harmful to human, causing respiratory diseases, and leading to death.

Catalytic ozone decomposition will decompose ozone to non-lethal compound, which is oxygen. Either metal or metal oxide is used for active sites of catalyst. Metal that can be used for catalyst are platina and palladium, whereas for metal oxide are manganese oxide, cobalt oxide, nickel oxide, silver oxide, and zinc oxide [3]. ZnO is chosen for this investigation because it is cheap and has good catalytic activity [4]. Catalyst support is used to get higher conversion of ozone decomposition. GAC is used as a support because it is a good adsorbent and has large specific surface area. With larger surface area, ZnO is easier to be dispersed onto the support and the amount of ZnO active sites will increase on catalyst support. Moreover, GAC also has oxygen functional groups in its structure which also can be used as catalyst for ozone decomposition [5].

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2. Methodology/Experimental

2.1. Samples
All chemicals were analytical grade reagents and used as received without further purification. GAC was obtained from CV Ady Water, Jakarta. Deionized water, HCl, NaOH, H$_2$SO$_4$, KI, and Na$_2$S$_2$O$_4$ and were obtained from CV Sinar Kimia, Tangerang. ZnCO$_3$ was obtained from CV Inti Periodik Laboratory, Bogor. Tetra cloth for mask filter was supplied from CV Cahaya Textile, Bogor. Mask was supplied from houseware store in Asemka, Jakarta.

2.2. Preparation of ZnO/GAC
Three sizes of GAC were used for this investigation, which were 18 – 35 mesh, 35 – 60 mesh, and 60 – 100 mesh. GAC was pre-treated with 1 mol/L HCl and 1 mol/L NaOH to remove impurities on the surface. Then, the treated GAC was impregnated in ZnCO$_3$ solution for 12 hours with loading percentage of 0 – 2%-w. After impregnated, ZnO/GAC was calcined at 300 °C for 30 minutes to release CO$_2$.

2.3. Characterization of ZnO/GAC
Specific surface area was determined by BET method using nitrogen adsorption at the boiling temperature of liquid nitrogen. ASAP 2020 by Micromeritics was used for BET instrument. Surface morphology of ZnO/GAC was observed by scanning electron microscopy (SEM) and composition was analyzed by energy dispersive X-ray spectroscopy (EDX). Instrument JEOL JSM 6510L A was used for SEM-EDX. The magnitude for SEM was 1.000x and the voltage was 20 kV. The accelerating voltage for EDX was 20 kV and the energy range for EDX was between 0 – 20 keV. Crystal phase was studied by X-ray diffraction (XRD). Empyrean XRD was used for the instrument within a diffraction interval 2θ of 5 – 80 degrees.

2.4. Catalytic Activity Test
Catalytic activity was investigated using fixed bed reactor which has radius of 10 cm and length of 1 cm. Commercial ozone generator was used to produce ozone from air with concentration of 23.28 mg/hour and flow rate of 2.39 L/minute. Excess of ozone from ozone decomposition reaction was analyzed using iodometric titration method. Amount of ozone was determined by reaction of ozone with iodine ion (I$^-$) which produces iodine (I$_2$) at acidic condition. Acidic condition was fulfilled by addition of H$_2$SO$_4$. I$_2$ was titrated with sodium thiosulfate (Na$_2$S$_2$O$_4$) and volume of Na$_2$S$_2$O$_4$ was used to calculate the volume of ozone which had not been decomposed to oxygen.

3. Results and Discussion
Surface morphology and composition of GAC before and after being pre-treated was showed in figure 1, figure 2, and table 1. Figure 1 and table 1 displayed that there were many impurities on the surface of GAC before pre-treatment. Therefore, by having a pre-treatment using strong acid and strong base solution, impurities were removed because there were ion exchange on catalyst. Aqueous HCl solution were dissolved and chloride ion (Cl$^-$) was bonded with any positive charged impurities. Meanwhile, hydrogen ion (H$^+$) was bonded with GAC. With the addition of NaOH, H$^+$ from strong acid solution then bonded with hydroxide ion (OH$^-$) and formed water, while sodium ion (Na$^+$) was bonded with negative charge impurities. From Table 1, it could be seen that the composition of Na, O, and Al were increase. Na and O were on the surface of GAC because the use of NaOH as pre-treatment solution, whereas Al was increase because the use of aluminum foil and aluminum tray when drying catalyst in the oven.
Figure 1. SEM analysis of GAC before pre-treatment.

Figure 2. SEM analysis of GAC after pre-treatment.

| Catalyst Composition | Before pre-treatment (%) | After pre-treatment (%) |
|----------------------|--------------------------|-------------------------|
| C        | 81.34        | 79.38        |
| O        | 9.42         | 17.53        |
| Na       | 0.75         | 2.02         |
| Mg       | 0.10         | 0.00         |
| Al       | 0.00         | 0.44         |
| Si       | 0.13         | 0.00         |
| P        | 0.50         | 0.00         |
| Cl       | 1.50         | 0.00         |
| K        | 3.39         | 0.00         |
| Ca       | 0.00         | 0.63         |
| Fe       | 2.56         | 0.00         |
| Mo       | 0.31         | 0.00         |

Pore volume and surface area of GAC values were showed in Table 2. These data were obtained using BET characterization method. It could be seen from the Table that pore volume and surface area were increase after pre-treatment. With larger surface area, ZnO would be easier to be dispersed onto GAC and conversion of ozone decomposition could be increased.

| Parameter                  | GAC 18 – 35 mesh | GAC 35 – 60 mesh | GAC 60 – 100 mesh |
|----------------------------|------------------|------------------|-------------------|
| Pore volume (cm$^3$/g)     | Before | After | Before | After | Before | After |
|                            | 0.130     | 0.427   | 0.157  | 0.447  | 0.184  | 0.478  |
| Surface area (m$^2$/g)     | 244.29   | 801.02  | 288.92 | 842.24 | 333.54 | 906.21 |

Table 3 showed the nominal value of Zn in catalyst after impregnation. Catalysts with 1%-w loading had a lower nominal value than the expected loading. Meanwhile, for 2%-w, all values were higher than the wanted loading. It could be happen because ZnCO3 is an insoluble solid and can make the agitation process in impregnation become uneven to the surface of GAC. The used of electron in SEM-EDX method was focusing in one point of catalyst, so the nominal value could not represent the loading percentage of catalyst.
| Size of GAC (mesh) | Percentage in 1% -w loading (%) | Percentage in 2% -w loading (%) |
|-------------------|-------------------------------|-------------------------------|
| 18 – 35           | 0.73                          | 3.84                          |
| 35 – 60           | 0.05                          | 2.62                          |
| 60 – 100          | 0.98                          | 3.50                          |

Table 3. Nominal value of ZnO in GAC

Figure 3 displayed a peak comparison between ZnCO3/GAC catalyst before calcined and Smithsonite solid (ZnCO3) (JCPDS 8-0449). Smithsonite solid has peaks located at 25°, 32°, 35°, 38°, 42°, 46°, 51°, and 53° with peaks at 25° and 32° have higher intensity than other peaks. From the Figure, it could be seen that catalyst also had a peak at 25° with intensity of 600 counts and peak at 32° with intensity of 100 counts. Both peaks indicated the presence of ZnCO3 structure in catalyst.

From XRD result, catalyst did not show specific peaks like Smithsonite solid. This happened because GAC is an amorphous solid whose particles are arranged unevenly. This make the length between atoms becomes irregular and will lead a structural aberration that shows unspecific peaks.

Figure 4 showed a peak comparison between ZnO/GAC catalyst after calcined and Zincite solid (ZnO) (JCPDS 36-1451) which also depicted with blue and red. Zincite solid has peaks located at 31°, 34°, 36°, 47°, and 56° with peaks at 31° and 36° have higher intensity than other peaks. From the figure, it could be seen that catalyst also had peaks at 31°, 34°, and 36°, although the intensities were not really high. Peak at 31° had an intensity of 100 counts, peak at 36° had an intensity of 70 counts, and peak at 47° had an intensity of 80 counts. Despite the low intensities, it still could be concluded that there was a ZnO crystal structure in catalyst.

Characterization with XRD method on various size and loading percentage of catalysts concluded in figure 5. Catalysts with 2%-w loading had higher intensity at 31°, 34°, and 36° peaks compared to 1%-w loading. Those three peaks indicated the presence of ZnO in catalysts. With bigger loading of ZnO, X-ray would be frequently hit the ZnO structure thus made the intensity of the specific peaks higher.
Figure 4. XRD analysis of ZnO$_3$/GAC catalyst after calcination.

Figure 5. XRD analysis upon various size and loading percentage of catalysts.

Figure 6 and figure 7 showed the conversion of ozone to oxygen for GAC catalysts before and after pre-treatment. Catalysts before pre-treatment had the lowest conversion because impurities were still remained on the surface of GAC. Impurities covered the active sites of catalyst so the surface for ozone decomposition reaction was less than GAC after pre-treatment. Also from both figures, it could be seen that the smallest size of GAC (60 – 100 mesh) had the best catalytic activity compared to any larger sizes. Size of catalyst supports affected the performance of the catalyst because with smaller size used, there were more active sites for ozone to be decomposed to oxygen.
Figure 6. Conversion of ozone decomposition for GAC before pre-treatment.

Figure 7. Conversion of ozone decomposition for GAC after pre-treatment.

Figure 8 and figure 9 displayed the conversion of ozone to oxygen for ZnO/GAC catalyst with 1 and 2%-w consecutively. Addition of ZnO in catalyst gave a great impact to the conversion of ozone decomposition. It could be seen from the figure that the conversion was increased significantly when using catalysts with 1 – 2%-w loading and 2%-w loading showed the biggest conversion. Higher conversion after adding ZnO onto the catalysts occurred because the characteristic of ZnO as a donor and acceptor. ZnO had many defect sites like oxygen vacancies [4]. Oxygen vacancies were important parts of ZnO structure because those were the place for ozone to be absorbed and oxygen to be desorbed from catalysts. When ozone molecule was on the surface of catalyst, one oxygen atom from ozone would fill the oxygen vacancies in ZnO and leave the oxygen gas to be released from catalysts [6].

Figure 8. Conversion of ozone decomposition for ZnO/GAC 1%-w loading.

Figure 9. Conversion of ozone decomposition for ZnO/GAC 2%-w loading.

4. Conclusion

Decomposition of ozone could be done effectively using ZnO catalyst with GAC support. ZnO/GAC catalyst had high value of conversion for all sizes and loading percentages. ZnO/GAC catalyst with size of 60 – 100 mesh and loading percentage of 2%-w had the highest conversion value which was reached 100% for 30 minute process.
Size and loading percentage of the catalyst had a relationship with the conversion of ozone in which the smaller size of a catalyst made ZnO easily dispersed to the support and higher percentage of ZnO means more defect sites or oxygen vacancies which could convert more ozone to oxygen molecules.

5. Acknowledgement

The authors acknowledge Universitas Indonesia and PITTA-UI 2017 program for the financial support. We are also thankful to Badan Tenaga Nuklir Nasional and FMIPA Universitas Negeri Jakarta for the instruments to characterize the catalysts.

6. References

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