

Comparative study of activated carbon, natural zeolite, and green sand supports for CuO_x and ZnO sites as ozone decomposition catalyst

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Abstract. This research was based on ozone decomposition in industrial environment. Ozone is harmful to human. Therefore, catalysts were made as a mask filter to decompose ozone. Comparison studies of catalyst supports were done using Granular Activated Carbon (GAC), Natural Zeolite (NZ), and Green Sand (GS). GAC showed the highest catalytic activity compared to other supports with conversion of 98%. Meanwhile, the conversion using NZ was only 77% and GS had been just 27%. GAC had the highest catalytic activity because it had the largest pore volume, which is $0.478 \text{ cm}^3/\text{g}$. So GAC was used as catalyst supports. To have a higher conversion in ozone decomposition, GAC was impregnated with metal oxide as the active site of the catalyst. Active site comparison was made using CuO_x and ZnO as the active site. Morphology, composition, and crystal phase were analyzed using SEM-EDX, XRF, and XRD methods. Mask filter, which contained catalysts for ozone decomposition, was tested using a fixed bed reactor at room temperature and atmospheric pressure. The result of conversion was analyzed using iodometric method. CuO_x/GAC and ZnO/GAC 2%-w showed the highest catalytic activity and conversion reached 100%. From the durability test, CuO_x/GAC 2%-w was better than ZnO/GAC 2%-w because the conversion of ozone to oxygen reached 100% with the lowest conversion was 70% for over eight hours.

1. Introduction

Ozone is commonly used in many industries. Ozone is a strong oxidizing agent in the disinfection process, which not only removes bacteria, viruses, and germs, but also improves the quality of water and preserves food [1]. However, some industries do not have an ozone destructor unit and the excess of ozone is released into the air and have reached 0.1 – 0.4 ppm, which exceeds the allowed threshold [2], [3]. The allowed threshold for ozone is 0.1 ppm in 8 hours (REL, Recommended Exposure Limits). High concentration ozone is harmful to human, causing respiratory diseases, and leading to death.

Catalytic ozone decomposition is preferred because it can be operated at room temperature [4]. Active sites of the catalysts have either metal or metal oxide. CuO_x and ZnO were chosen as the variation of the active sites for this research because those have good catalytic activity for ozone decomposition and have been used commercially [5]. Catalyst support used to increase the conversion

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of ozone decomposition. The presence of a catalyst support with a high surface area can improve the catalytic activity of catalysts such as Granular Activated Carbon (GAC), Natural Zeolite (NZ), and Green Sand (GS). All of them have high adsorption ability and a wide surface area. With a wider surface area, active sites of metal oxide are easier to be dispersed on the catalyst support.

2. Methodology/ Experimental

2.1. Material

All chemicals were analytical grade reagents and used as received without further purification. GAC and NZ were obtained from CV Ady Water. GS was obtained from CV Mitra Water. Deionized water, HCl, NaOH, H₂SO₄, KI, and Na₂S₂O₄ and were obtained from CV Sinar Kimia. CuCO₃ was obtained from PD Cipta Bangun Nauli. ZnCO₃ was obtained from Inti Periodik Laboratory. Tetra cloth for mask filter was supplied from CV Cahaya Textile. Mask was supplied from Asemka.

2.2. Instrumentation

Instruments that used to investigate the catalytic activity were fixed bed reactor and commercial ozone generator. X-Troy Ozonator was used to produce ozone. ASAP 2020 by Micromeritics was used for BET analysis. JEOL JSM 6510L A was used for SEM-EDX analysis. TORONTECH TT-EDXPRT was used for XRF analysis. Empyrean XRD was used for XRD analysis.

2.3. Procedure

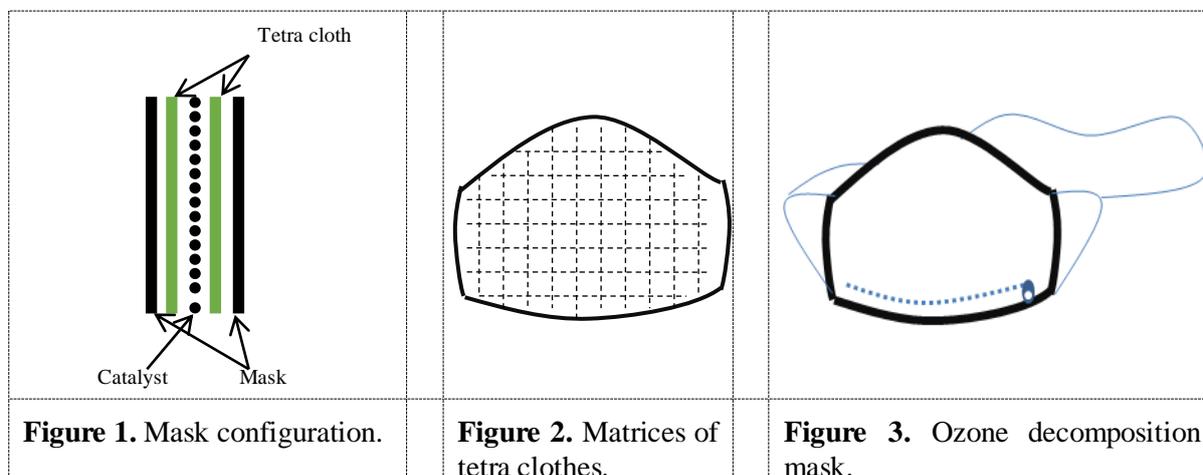
2.3.1. Preparation and characterization of catalyst support GAC, NZ, and GS with size of 18 – 100 mesh were used for investigation. First, GAC, NZ, and GS were pre-treated with 0.05 mol/L HCl and 0.05 mol/L NaOH both for an hour to remove the impurities or ash content on the surface.

2.3.2. Impregnation of catalyst The best catalyst support which has the highest catalytic activity and widest surface area was impregnated to CuCO₃ and ZnCO₃ solutions for 12 hours with loading percentage of 0-2%-w. After impregnated onto the catalyst support, catalysts were calcined at 300 °C for 1 hour to release CO₂.

2.3.3. Catalytic activity test Catalytic activity of the samples was investigated using a fixed bed reactor with a diameter of 10 cm and height of 1 cm. Catalyst with mass of 10 grams was used for investigation. Operating conditions of the reactor were room temperature and atmospheric pressure. Commercial ozone generator was used to produce ozone from air with concentration of 0.388 mg/minute. Excess of ozone from the reaction was analyzed using iodometric titration method. The amount of ozone was determined by reaction of I⁻ ion with ozone, which produces iodine (I₂) at acidic condition. Acidic condition was fulfilled by the addition of H₂SO₄. Then, I₂ was titrated with sodium thiosulfate (Na₂S₂O₄) at pH 2 (± 10%) and the volume of Na₂S₂O₄ could be used to calculate the volume of ozone which had not yet been decomposed to oxygen.

2.3.4. Characterization of catalyst Treated catalyst supports were observed by BET method to determine pore volume and specific surface area. Before measurements, samples were degassed at 300 °C. Surface morphology of catalysts was observed by scanning electron microscopy (SEM) and surface composition analysis was carried out by energy dispersive X-ray spectroscopy (EDX) and X-Ray Fluorescence (XRF). The magnitude for SEM was x1.000 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. XRF used soil method. Crystal phase was studied by X-ray diffraction (XRD) with diffraction interval 2θ of 5 – 80°.

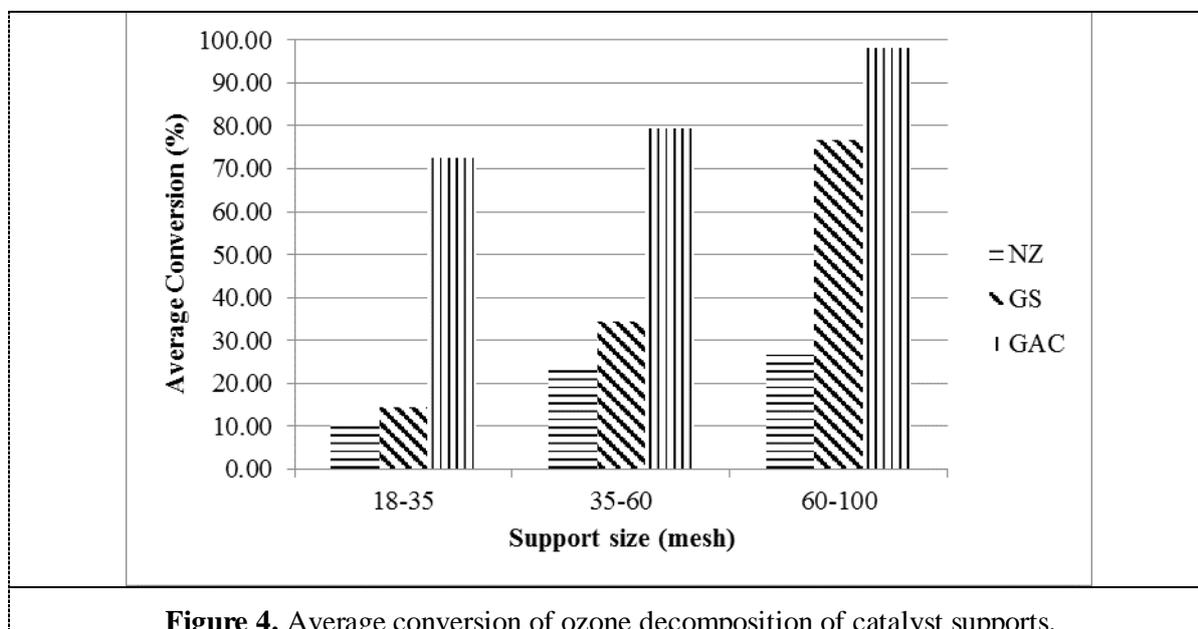
2.3.5. Mask preparation Two pieces of tetra cloth with a size of 20 x 12 cm were filled with catalyst and stitched to form 1x1 matrices. Tetra clothes which were used as a mask filter was inserted into a mask which already contained a zipper.



3. Results and Discussion

3.1. Catalytic activity analysis of catalyst support

Figure 4 showed that GAC with a size of 60 – 100 mesh had the highest conversion compared to other supports and sizes. Catalyst supports with smaller size (60 – 100 mesh) had the largest surface area for ozone to be decomposed to oxygen. GAC also had oxygen functional groups that can be used to decompose ozone [6].



3.2. BET analysis of catalyst support

Specific surface area and pore volume of GAC, NZ, and GS with a size of 60-100 mesh could be seen in Table 1. It showed that there was an increase in surface area and pore volume for GAC. But,

contrary to GAC, surface area and pore volume for NZ and GS were decreased. These were occurred because of desilication. Desilication happened when silica was dissolved during NaOH treatment and the outer layer of the structure shrunk. Partial dealumination also happened because of HCl treatment. When desilication and dealumination occurred at a serious level, the structure of the catalyst would be deformed and decrease the surface area [7].

Meanwhile, surface area and pore volume increased for GAC because impurities on the surface were removed. Aqueous HCl solution was dissolved and Cl^- ion was bonded with any positive charged impurities and H^+ ion bonded with GAC. With the addition of NaOH, H^+ ion, which was previously bonded with GAC, then bonded with OH^- ion and formed water, while Na^+ ion was bonded with negative charge impurities. Excess of Na^+ was bonded to GAC. Because GAC had the highest surface area and pore volume, it was used for the catalyst support of CuO_x and ZnO.

Table 1. BET characterization of catalyst support.

Parameter	GAC		NZ		GS	
	Before pre-treatment	After pre-treatment	Before pre-treatment	After pre-treatment	Before pre-treatment	After pre-treatment
Pore volume (cm^3/g)	0.184	0.317	0.092	0.093	0.049	0.015
Surface area (m^2/g)	333.545	558.754	53.334	40.931	55.563	5.574

3.3. Catalytic activity analysis for CuO_x/GAC and ZnO/GAC

Comparison of catalyst activity between CuO_x/GAC and ZnO/GAC catalyst at different loading percentage could be seen in Figure 5. It turned out that both catalysts have the same average conversion value in the first 30 minutes. The catalyst with loading 1%-w and 2%-w had a perfect ozone conversion which was 100%.

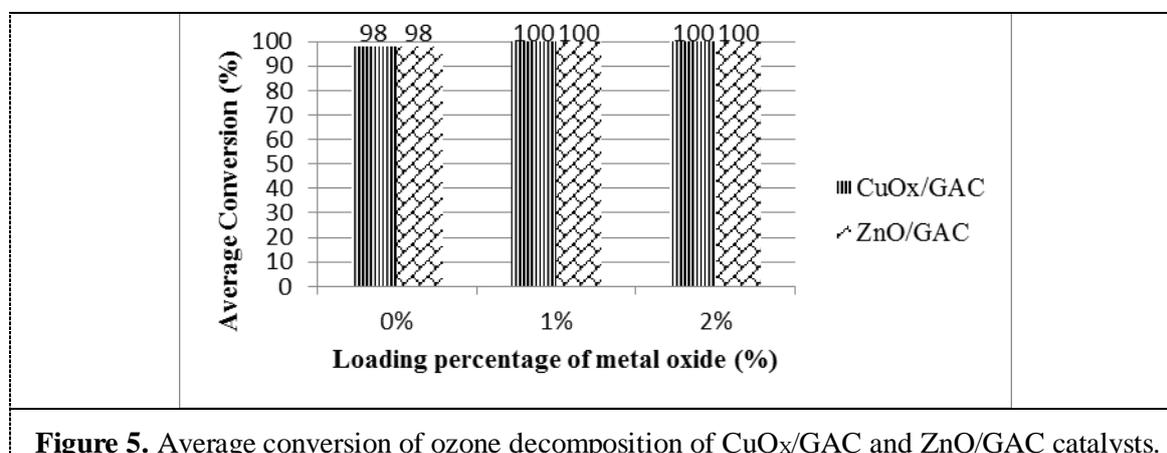


Figure 5. Average conversion of ozone decomposition of CuO_x/GAC and ZnO/GAC catalysts.

Based on the literature, CuO_x had a conversion of ozone decomposition, which was 21 – 22% [8]. Therefore, doping of CuO_x to catalyst support increased catalytic activity significantly. Another literature explained that when the content of CuO_x increased from 1%-w to 5%-w, the catalytic activity was increased. However, further increasing the CuO_x content to 7%-w and 9%-w resulted in a decrease of the catalytic activity. From literature, CuO_x with 5%-w loading exhibited the highest catalytic activity [9]. Meanwhile, for the previous research of ZnO catalyst for ozone decomposition, conversion only reached 30% at room temperature [10]. Nevertheless, by increasing the loading of ZnO in catalysts, would increase the defect sites in catalysts. Defect sites such as oxygen vacancies were important parts of ZnO structure because oxygen vacancies were the place of ozone decomposition occurred [11].

3.4. Characterization of CuO_x/GAC and ZnO/GAC

3.4.1. SEM-EDX analysis Surface morphology and composition of GAC before and after pre-treatment were shown in Figure 6, Figure 7 and Table 2. From Table 2, it could be concluded that many impurities existed on the surface of GAC before pre-treatment. The amount of impurities such as Mg, Fe, Cl, Ca, and K decreased after pre-treatment. Amount of Na was increased because NaOH had been used in pre-treatment and bonded to GAC surface.

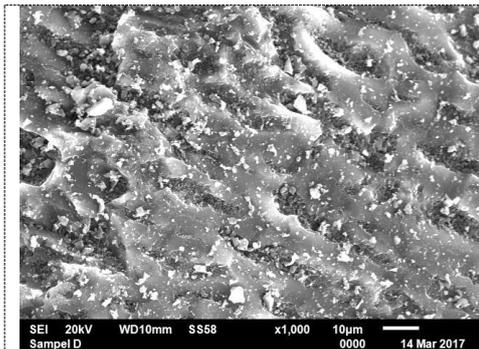


Figure 6. SEM analysis of GAC before pre-treatment.

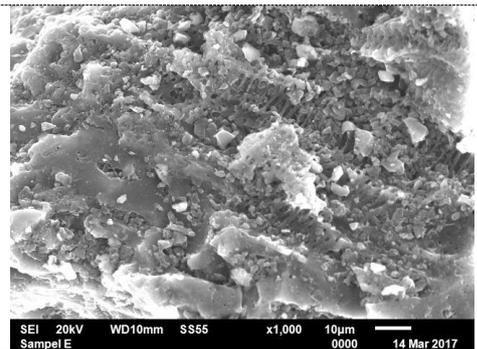


Figure 7. SEM analysis of GAC after pre-treatment.

With a wider surface area, CuO_x would be easier to be dispersed into the GAC. Figure 8-11 displayed the surface morphology of CuO_x/GAC and ZnO/GAC 1-2%-w.

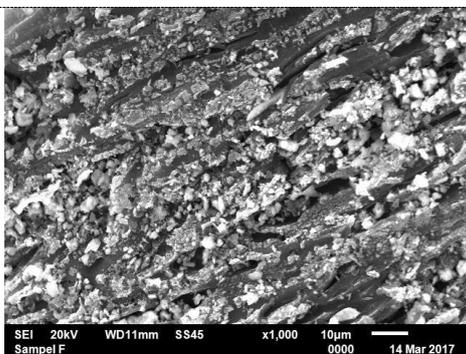


Figure 8. SEM analysis of CuO_x/GAC 1%-w.

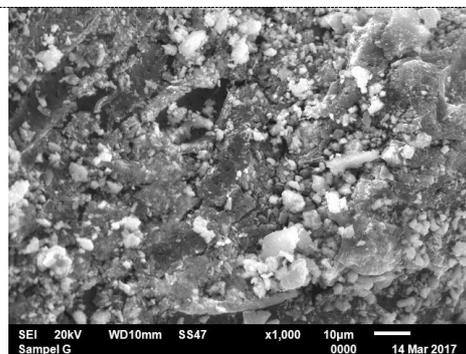


Figure 9. SEM analysis of CuO_x/GAC 2%-w.

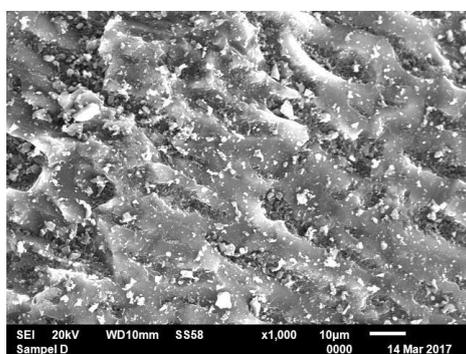


Figure 10. SEM analysis of ZnO/GAC 1%-w.

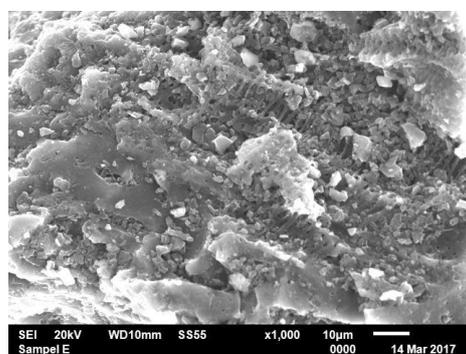


Figure 11. SEM analysis of ZnO/GAC 2%-w.

Table 2 also gave data of Cu and Zn on GAC that have been impregnated. It seems that the composition of Cu and Zn in any samples did not match the loading percentage. EDX only analyzed some chemical elements that were several microns from the surface of the catalyst. With higher amount of Cu and Zn, metal oxides were not absorbed into the pores of the GAC and just attached to the outer surface of the GAC. Because GAC possessed a very small micropore size, metal oxide particles were hardly accessed the micropore and only attached to the outer surface, not the deepest pore. Moreover, EDX methods only shot at one sample point, not analyzed all the surface of the catalyst.

Table 2. EDX characterization of GAC before and after impregnation.

Composition	Before pre-treatment (%)	0%-w	CuO _x /GAC		ZnO/GAC	
			1%-w	2%-w	1%-w	2%-w
C	81.34	78.89	70.89	73.09	77.91	72.74
O	9.42	17.53	20.63	14.07	20.23	21.46
Na	0.75	2.02	1.78	0.00	0.00	0.00
Mg	0.10	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.44	0.00	0.00	0.00	0.29
Si	0.13	0.00	0.00	0.00	0.00	0.00
P	0.50	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.34	0.56	0.98	3.50
Cl	1.50	0.00	0.00	0.00	0.00	0.23
K	3.39	0.00	0.00	0.00	0.00	1.76
Cu	0.00	0.00	6.19	12.16	0.00	0.00
Ca	0.00	0.63	0.17	0.00	0.88	0.00
Fe	2.56	0.00	0.00	0.00	0.00	0.00
Mo	0.31	0.00	0.00	0.00	0.00	0.00

3.4.2. XRD analysis Figure 12 and Figure 13 consecutively showed the XRD analysis of CuO_x/GAC before and after calcined and Table 3 showed the intensity. JCPDS 76-660, JCPDS 65-2309, JCPDS 05-0667 were used as references for CuCO₃, CuO, and Cu₂O. It showed that there was a decrease in peak position after calcined process. Calcined process decomposed CO₂ from CuCO₃ to create CuO_x. From XRD analysis, after calcined, only CuO_x (CuO and Cu₂O) remained in GAC.

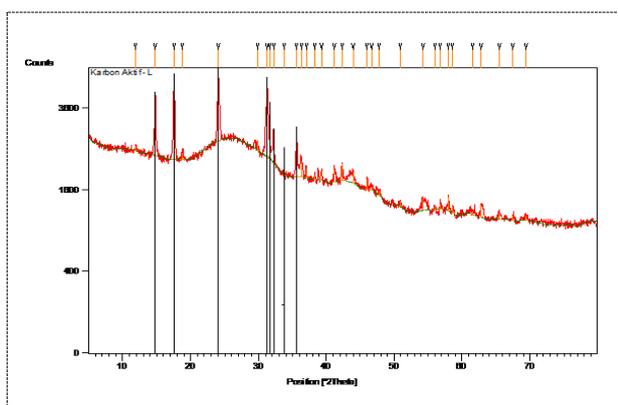


Figure 12. XRD analysis of CuO_x/GAC 1%-w.

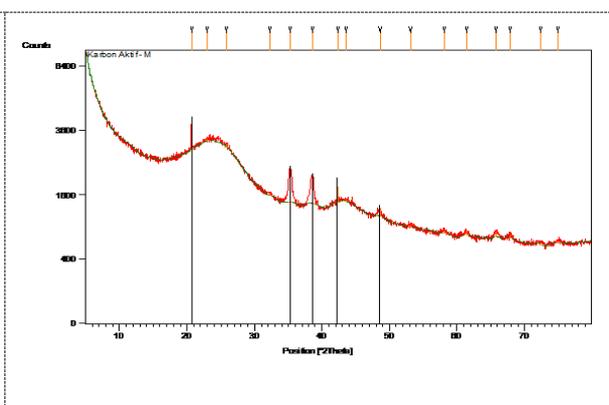
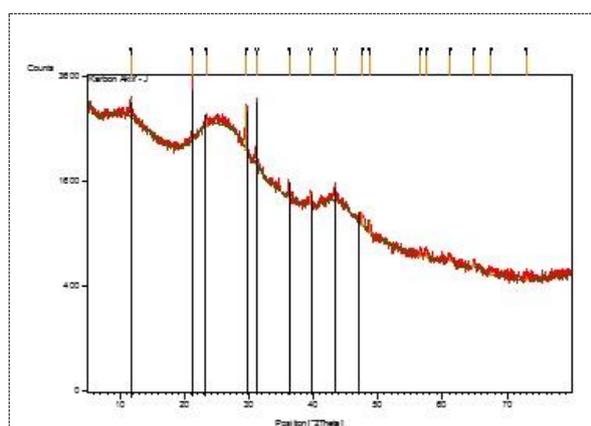
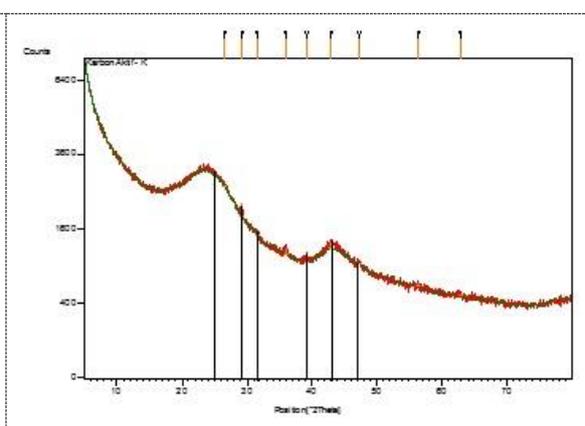


Figure 13. XRD analysis of CuO_x/GAC 2%-w.

Table 3. XRD peak list of CuO_x/GAC.

Before calcined			After calcined			
Compound	2θ (°)	Rel. Intensity (%)	Compound	2θ (°)	Rel. Intensity (%)	
CuCO ₃	14.7756	62.29	CuO	35.2256	100.00	
	17.5614	86.46			38.6532	79.66
	24.0875	97.95	Cu ₂ O	42.3340	43.34	
	31.2850	100.00				
	31.6315	69.99				
	32.1952	38.91				
	35.5834	49.00				

Figure 14 and Figure 15 displayed the XRD analysis of ZnO/GAC before and after calcined and Table 4 showed the intensity. JCPDS 8-0449 and JCPDS 36-1451 were used consecutively as references for ZnCO₃ and ZnO. It seems that there was a decrease in peak position after calcined process. This process also decomposed CO₂ from ZnCO₃ to create ZnO. From XRD analysis, after calcined, only ZnO remained in GAC.

**Figure 14.** XRD analysis of ZnO/GAC 1% -w.**Figure 15.** XRD analysis of ZnO/GAC 2% -w.**Table 4.** XRD peak list of ZnO/GAC.

Before calcined			After calcined			
Compound	2θ (°)	Rel. Intensity (%)	Compound	2θ (°)	Rel. Intensity (%)	
ZnCO ₃	11.6863	44.39	ZnO	26.5884	23.03	
	21.1760	77.81			29.2305	100.00
	23.3473	15.40			31.5557	17.78
	29.5453	100.00			39.2556	34.16
	31.1068	64.92			42.9412	24.26
	36.1921	17.73			47.2526	37.45
	39.5114	21.77				
	43.3993	22.96				
	47.6005	19.23				

3.4.3. XRF analysis XRF method was used to see the metal oxide composition in GAC after impregnation. Table 5 showed the loading percentage of CuO_x and ZnO. CuO_x 2%-w had a near-real value, while CuO_x 1%-w was greater than the desired loading percentage. This could happen because the impregnation process was uneven, so the loading on the GAC was not homogeneous. Additionally, ZnO 1%-w and 2%-w have less value than the desired loading percentage. This might be due to agitation process that was not perfect, so ZnO did not attach to the whole GAC.

Table 5. XRD peak list of ZnO/GAC.

Catalysts	Loading percentage	
	1%-w	2%-w
CuO _x /GAC	1.66	1.90
ZnO/GAC	0.47	1.58

3.5. Catalyst durability

CuO_x/GAC and ZnO/GAC catalysts were tested for 8 hours. The results could be seen in Figure 16.

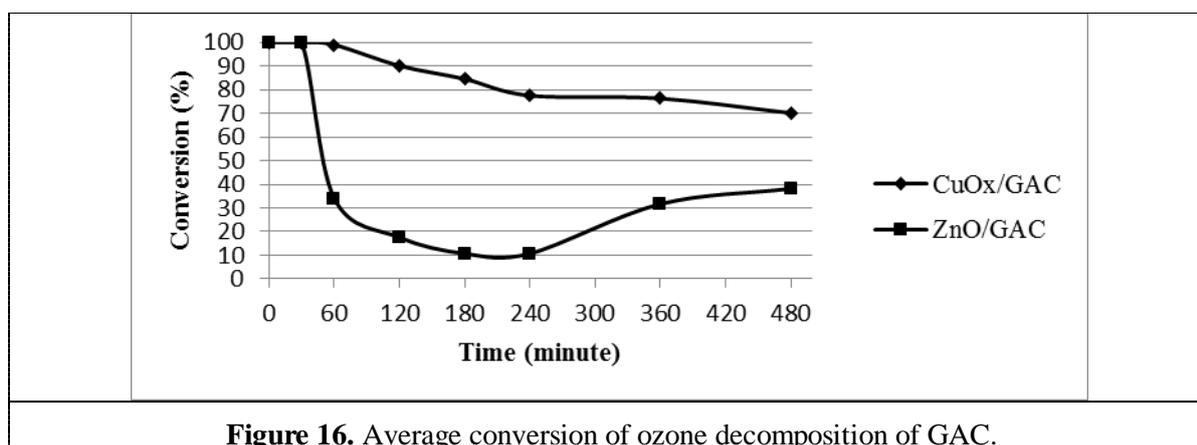


Figure 16. Average conversion of ozone decomposition of GAC.

CuO_x/GAC catalyst performance was better than ZnO/GAC because it produced the highest ozone conversion. ZnO/GAC conversion decreased significantly after 30 minutes while CuO_x/GAC catalyst was after 60 minutes. There was a slight decrease in the conversion of CuO_x/GAC catalyst from 240 minutes to 360 minutes. It happened because the data were taken discretely, which was tested for 2 days. There was a 15-hour break after 240 minutes before the catalyst was tested again. It means that the catalyst was allowed to regenerate for 15 hours. This break gave time to O₂ and CO₂ to desorb from the catalyst. So, for the next day, the surface of the catalyst would be wider to decompose ozone. While for ZnO/GAC catalyst, after 240 minutes, conversion was increased. It also happened because of a 15-hour break. O₂ gas near the catalyst was bonded with the catalyst to make other oxygen functional group that could be used to decompose ozone. The use of mask to decompose ozone is important to our community because it decomposed ozone at least 75.45 ppm for CuO_x/GAC catalyst and 11.57 ppm for ZnO/GAC catalysts. Therefore, mask that contained CuO_x/GAC and ZnO/GAC can be used to reduce the ozone concentration to be below the allowed threshold.

4. Conclusion

The best catalyst support was GAC with a size of 60-100 mesh because it had the largest surface area and pore volume, which was 558.754 m²/g and 0.317 cm³/g. CuO_x/GAC and ZnO/GAC catalysts with loading 1%-w and 2%-w resulted in the highest conversion of 100% within the first 30 minutes.

However, CuO_x/GAC catalysts with loading percentage of 2%-w had the best catalyst activity because it could convert ozone to oxygen with a minimum of 70% within 8 hours.

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References

- [1] O'Donnell C, Tiwari B K, Cullen P J, Rice G 2012 *Ozone in Food Processing* (UK: John Wiley & Sons, Ltd.).
- [2] Subrahmanyam C, Bulushev D A, Kiwi-Minsker L 2005 *Applied Catalysis B: Environmental* **61** 98-106.
- [3] McKee D 1993 *Tropospheric Ozone: Human Health and Agricultural Impacts* (USA: CRC Press, Inc.).
- [4] Sigmund J 2001 *Catalytic Destruction of Ozone: A Cost Effective Approach to Controlling Off-Gas Ozone Emissions* (USA: EIJ Company LLC).
- [5] Dhandapani B, Oyama S T 1997 *Applied Chemistry B: Environmental* **11** 129-166.
- [6] Wang M, Zhang P, Li J, Jiang C 2014 *Chinese Journal of Catalysis* **35** 335-341.
- [7] Ates A, Akgul G 2016 *Powder Technology* **287** 285-291.
- [8] Dan C, Popovici E J, Imre-Lucacia F, Popovici N, Marginean P, Silaghi-Dumitrescu I 2008 *Journal of Optoelectronics and Advanced Materials* **10** 2234-2236.
- [9] Zhao F, Gong M, Zhang G, Li J 2015 *Journal of Rare Earths* **33** 604-610.
- [10] Milenova K I, Nikolov P M, Kasabova N A, Avramova I A 2014 *Polish Journal of Chemical Technology* **16** 55-59
- [11] Zhu G, Zhu J, Jiang W, Zhang Z, Wang J, Zhu Y, Zhang Q 2017 *Applied Catalysis B: Environmental* **209** 729-737.
- [12] Gurrath M, Kuretzky T, Boehm H P, Okhlopko L B, Lisitsyn A S, Likholobov V A 2000 *Carbon* **38** 1241-1255.