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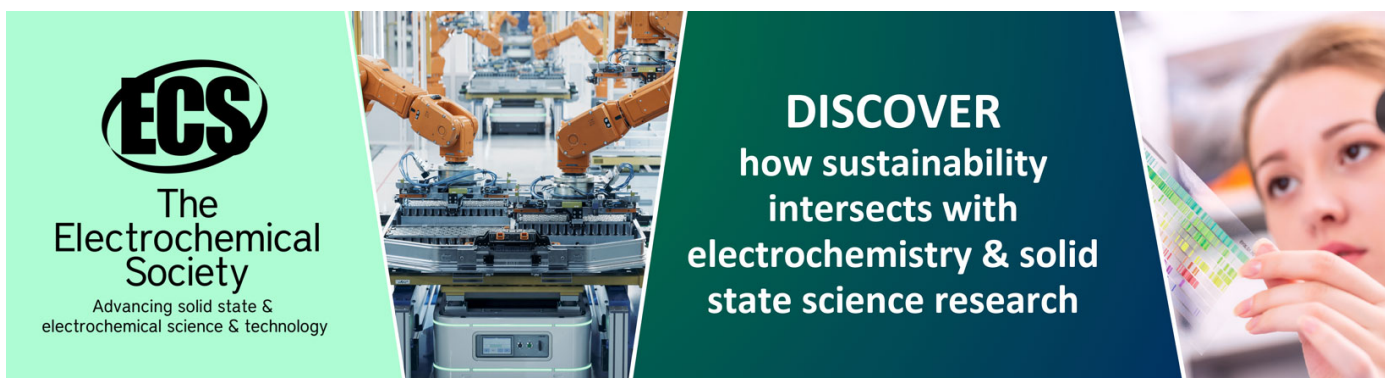
Preparation and characterization of copper oxide catalyst with activated carbon support for ozone decomposition in industrial environment

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Preparation and characterization of copper oxide catalyst with activated carbon support for ozone decomposition in industrial environment

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Abstract. In this research, ozone decomposition has been synthesized based on copper oxide (CuO_x) with granular activated carbon (GAC) as a support catalyst, being used as ozone decomposer in effluent gas emissions of industries that use ozone. Therefore, catalysts were made as a mask filter to decompose ozone. CuO_x was impregnated to the surface of GAC by using copper carbonate (CuCO_3) as precursor and then calcined to release carbon dioxide with temperature of 300 °C for 1 hour. Size of activated carbon and loading percentage of copper oxide to the support were varied to get the optimum value. The quality of a catalyst such as pore diameter and surface area are characterized by BET, the cross-sectional surface of the catalyst and the catalyst elements composition are analyzed by X-ray spectroscopy (SEM-EDX) and X-Ray Fluorescence (XRF), while CuO_x composition and crystal phase are analysed by XRD. Mask filter, which contained catalysts for ozone decomposition, was tested using a fixed bed reactor at room temperature and atmospheric pressure. Results of the catalytic conversion were tested using iodometric method. Activated carbon with smallest diameter (60 - 100 mesh) and highest loading percentage (2 %-wt) showed the highest activity which the ozone conversion to oxygen reached 100%. Amount of CuO_x on the support also determine the efficiency of catalyst due to appropriate amount of CuO_x probably maintain the morphology and crystal phase of the catalyst.

1. Introduction

Needs of catalyst for ozone decomposition are continue to increase. This can be happened because ozone is used in many industries, such as water treatment, antiseptic, air purifier, and food industries. Ozone is used because it is a strong oxidizing agent that can be used in the disinfection process, which can remove bacteria, viruses, germs, improve the quality of water, and preserve foods [1]. However, some industries do not have ozone destructor unit and the excess of ozone is released to the air and have reached 2000 ppm which is exceed the allowed threshold [2]. The allowed threshold for ozone is 0.1 ppm in 8 hours (Recommended Exposure Limits). This excess of ozone is harmful to human, causing respiratory diseases, and leading to death. Ozone decomposition with catalyst is preferred because it can operate at room temperature [3]. Active site of the catalyst has either metal or metal oxide. Metal that can be made as catalyst are Au, Pd, Ag, and Rh, whereas for the metal oxide are Mn, Cu, Cr, Co, Fe, Zn, and Ni. CuO_x is chosen for this research because it has high oxidation-reduction

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potential values and has been widely used commercially. CuO_x is a metal oxide that is often used as a catalyst in various reserches and has the ability in degradation [4]. But, to get higher conversion of ozone to be oxygen, catalyst needs a support. GAC is used as a support for the catalyst because of its wide specific surface area and its good adsorbent property. With wider surface area, CuO_x is easier to be dispersed on the support. GAC also has oxygen functional group in its structure, so it also can be used as catalyst for ozone decomposition [5].

2. Methodology/Experimental

2.1. Material

In this research used granular activated carbon (GAC) as support from coconut shell with three types of GAC size, which was 18-35 mesh, 35-60 mesh, and 60-100 mesh that were obtained from CV Ady Water in Jakarta. Aquades, HCl, NaOH, H_2SO_4 , KI, and $\text{Na}_2\text{S}_2\text{O}_4$ and were obtained from CV Sinar Kimia in Tangerang. CuCO_3 was obtained from PD Cipta Bangun Nauli in Bogor. Tetra cloth for mask filter was supplied from CV Cahaya Textile in Bogor. Mask was supplied from houseware store in Asemka.

2.2. Instrumentation

The instrument that used to investigate the catalyst activity was a fixed bed reactor (FBR) with an ozone was supplied from a 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 of CuO_x/GAC

Three types of GAC size was used for investigation, which was 18-35 mesh, 35-60 mesh, and 60-100 mesh and was derived from coconut shell. First, the GAC was pretreated with 1 mol/L HCl and 1 mol/L NaOH both for an hour to remove the impurities or ash content on the surface such as K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . Then, the treated GAC was impregnated in aqueous CuCO_3 solution for 12 hours by agitator with loading percentage of 0-2 %-wt. Loading percentage of CuO_x was calculated using the ratio of the CuO_x mass in the precursor solution to GAC. After impregnated onto the GAC, CuO_x/GAC was calcined at 300 °C for 1 hour to release the CO_2 .

2.3.2. Characterization of CuO_x/GAC

Specific surface area of GAC was determined by BET method using nitrogen adsorption at the boiling temperature of liquid nitrogen. Surface morphology of CuO_x/GAC were 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 1,000 times and the voltage was 20 kV. The accelerating voltage for EDX was 20 kV. XRF instrument used soil method. Crystal phase was studied by X-ray diffraction (XRD).

2.3.3. Catalytic activity test

Catalytic activity of the sample was investigated using a fixed bed reactor (FBR) whose radius was 10 cm and height was 1 cm. Catalyst with mass of 10 grams was used for investigation. Commercial ozone generator was used to produce ozone from air with concentration of 36 ppm in 1 L of air. Excess of ozone from the reaction was analyzed using iodometric titration method. Amount of ozone was determined by reaction of I^- ion with ozone which produces iodine (I_2) at acidic condition. Acidic condition was fulfilled by addition of H_2SO_4 . Then, I_2 was titrated with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_4$) at pH 2 and the volume of $\text{Na}_2\text{S}_2\text{O}_4$ could be used to calculate the volume of ozone which had not yet decompose to oxygen.

2.3.4. Mask preparation

Two pieces of tetra cloth with a size of 20 x 12 cm were filled with 10 grams of catalyst and stitched to form 1 cm x 1 cm matrices. Tetra clothes which were used as a mask filter were inserted into a

mask which already contained a zipper. Illustration of the mask showed in figure 1, figure 2, and figure 3.

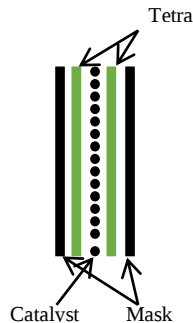


Figure 1. Mask configuration.

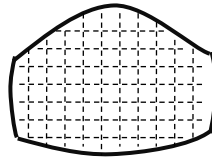


Figure 2. Matrices of tetra clothes.

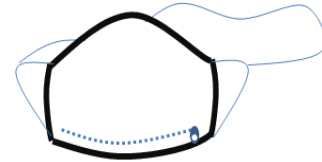


Figure 3. Ozone decomposition mask.

3. Results and Discussion

3.1. BET Analysis

Specific surface area of GAC was showed in table 1. It showed that there was an increase in specific surface area of the GAC because of the pre-treatment. Therefore, by having a pre-treatment for GAC using strong acid and strong base, impurities would be removed. Aqueous HCl solution were 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.

Table 1. BET characterization of GAC.

Parameter	GAC 18-35 mesh		GAC 35-60 mesh		GAC 60-100 mesh	
	Before pre-treatment	After pre-treatment	Before pre-treatment	After pre-treatment	Before pre-treatment	After pre-treatment
Pore diameter (nm)	2.12	2.13	2.15	2.12	2.20	2.11
Pore volume (cm^3/g)	0.130	0.427	0.157	0.447	0.184	0.478
Surface area (m^2/g)	244.29	801.02	288.92	842.243	333.54	906.21

3.2. SEM-EDX Analysis

Surface morphology and composition of GAC before and after being pre-treated was showed in Figure 4, figure 5, and table 2. Table 2 showed that there were many impurities in the surface of GAC before being pre-treated. The amount of impurities decreased after pre-treatment such as Mg, Fe, Cl, Ca, and K. It can be seen, that the amount of Na is increased because base treatment, where Na^+ was bonded to GAC surface.

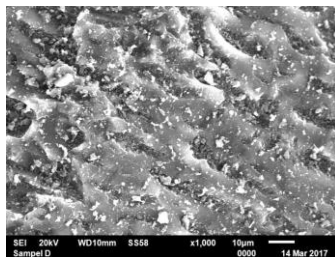


Figure 4. SEM analysis of GAC before pre-treatment.

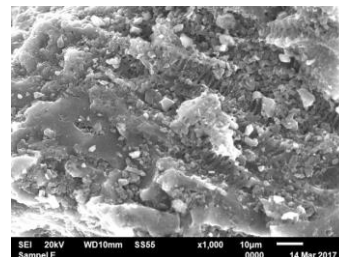
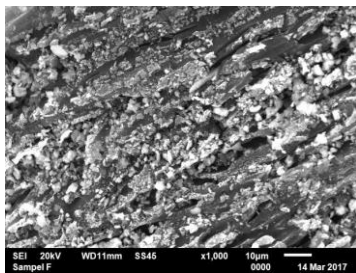
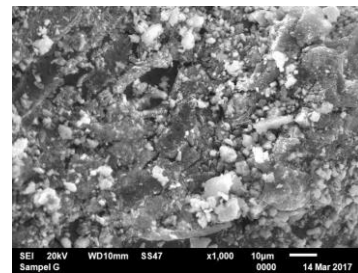


Figure 5. SEM analysis of GAC after pre-treatment.

Table 2. EDX characterization of GAC before and after pre-treatment.

Elements	Before pre-treatment (%-w)	After pre-treatment (%-w)
C	81.34	78.89
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
Zn	0.00	0.49
Cl	1.51	0.00
Ca	0.00	0.63
K	3.39	0.00
Cu	0.00	0.00
Fe	2.56	0.00
Mo	0.31	0.00
P	0.50	0.00

With wider surface area, CuO_x would be easier to be dispersed onto the GAC. Figure 6 and figure 7 showed the surface morphology of CuO_x /GAC for 1-2 %-wt.

**Figure 6.** SEM analysis of CuO_x /GAC 1%-w.**Figure 7.** SEM analysis of CuO_x /GAC 2%-w.

3.3. XRD Analysis

Figure 8 and figure 9 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 CuCO_3 , CuO , and Cu_2O . It showed that there were a decrease in peak position after calcined process. Calcined decomposed CO_2 from CuCO_3 to create CuO_x . From XRD analysis, after calcined, only CuO_x (CuO and Cu_2O) remained in GAC.

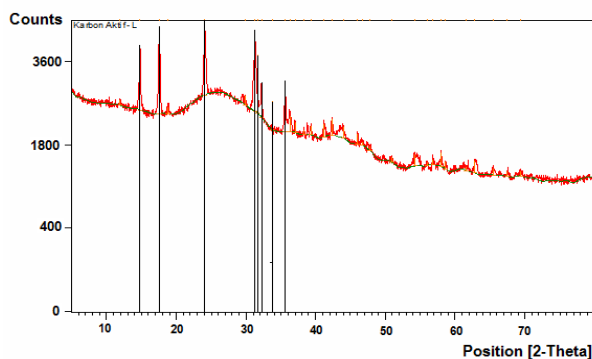
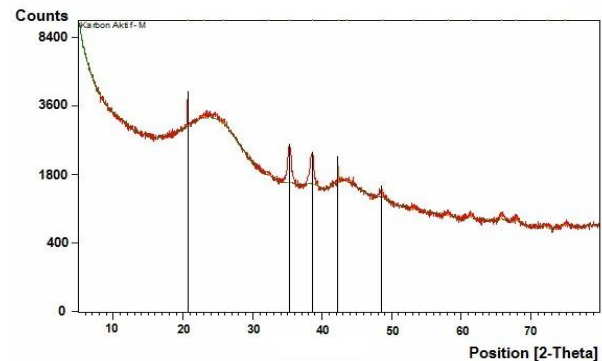
**Figure 8.** XRD analysis of CuO_x /GAC 1%-w.**Figure 9.** XRD analysis of CuO_x /GAC 2%-w.

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	Cu ₂ O	38.6532	79.66
	24.0875	97.95		42.3340	43.34
	31.2850	100.00			
	31.6315	69.99			
	32.1952	38.91			
	35.5834	49.00			

3.4. XRF Analysis

The XRF method was used to see the metal oxide compositions in GAC after impregnation. Table 4 showed the loading percentage of CuO_x at each size. The loading percentage of all catalysts had a near-real value, except CuO_x/GAC 1%-w 60-100 mesh 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.

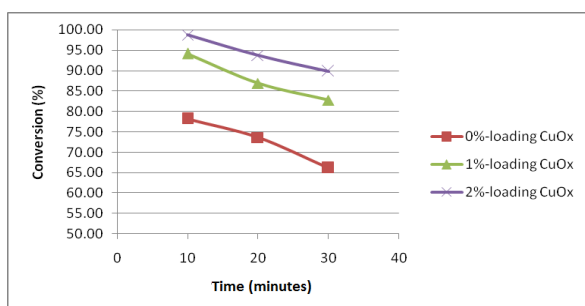
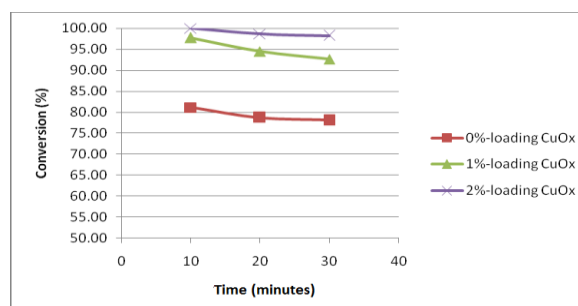
Table 4. %-loading CuO_x on GAC surface.

Size (mesh)	%loading	
	1%	2%
18-35	0.8 %	2.50 %
35-60	0.84 %	2.09 %
60-100	1.66 %	1.90 %

3.5. Catalytic Activity Analysis

Figure 10 showed the conversion of ozone to oxygen for CuO_x/GAC catalyst with size of 18-35 mesh. CuO_x/GAC that had been pre-treated had a capability to have high conversion value in ozone decomposition. From 30 minutes, GAC showed a decrease in the conversion of ozone to oxygen. GAC with size of 18-35 mesh and loading percentage of 1-2%-wt had an increase in conversion compared to loading 0%-wt. Figure 10 showed that higher loading of CuO_x would result a higher ozone conversion. With CuO_x/GAC catalyst, conversion of ozone into oxygen occurred not only because of the reaction of ozone with carbon, but also with CuO_x.

Figure 11 showed the conversion of ozone to oxygen for CuO_x/GAC catalyst with size of 35-60 mesh. When CuO_x/GAC had been pre-treated, performance of catalyst increased significantly. Up to 30 minutes, the conversion of ozone for CuO_x/GAC with size of 35-60 mesh and any loading percentage was higher than 90%. This high conversion of ozone also happened with CuO_x/GAC catalyst whose size was 60-100 mesh. This could be seen in figure 12.

**Figure 10.** Conversion of ozone as a function of time for some loadings of CuO_x/GAC 18-35 mesh.**Figure 11.** Conversion of ozone as a function of time for some loadings of CuO_x/GAC 35-60 mesh.

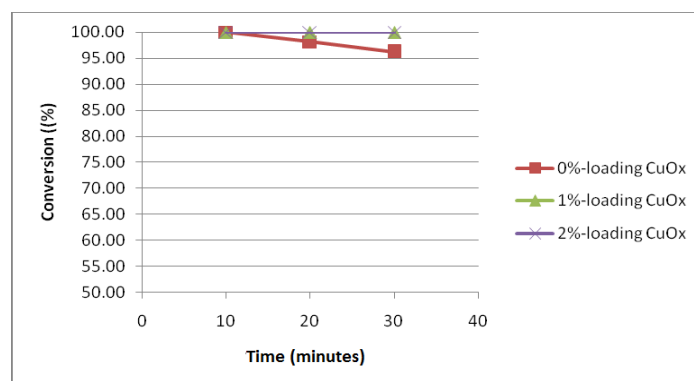


Figure 12. Conversion of ozone decomposition for CuO_x/GAC 60-100 mesh.

The presence of oxide of metal on the catalyst support increased the conversion of ozone to oxygen. In this case, the existence of CuO_x improved conversion rate of ozone by converting ozone to oxygen. The existence of CuO_x also extended the lifespan of the GAC. Appropriate amount of CuO_x gave an optimum value of active sites on the catalyst and maintained the morphology and crystal phase of the catalyst. Ozone might interact with CuO_x before reacted with carbon.

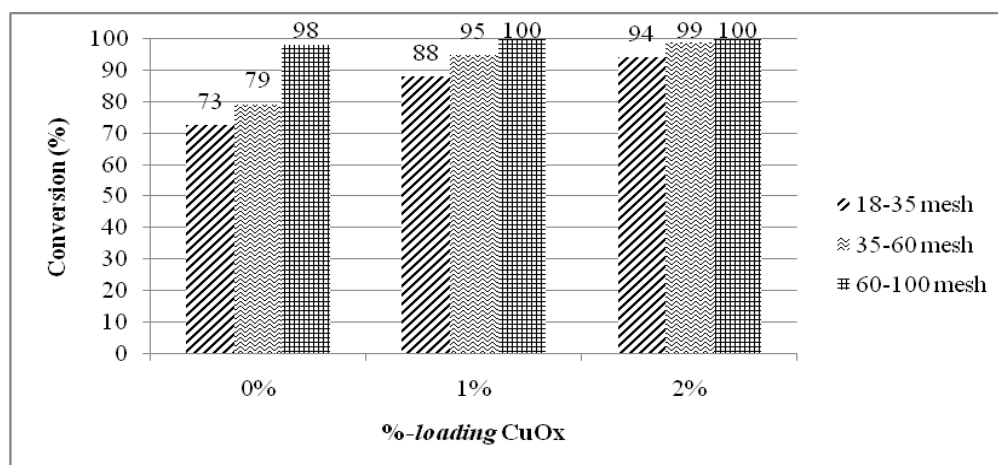


Figure 13. Ozone decomposition or conversion for various mesh of CuO_x/GAC catalysts.

Decomposition of ozone was very good at GAC 35-60 and 60-100 mesh 2%-wt. In addition to loading percentage and pre-treatment, this showed that the size of GAC had a very significant effect to ozone decomposition. Smaller size catalyst had larger surface area and bigger pore volume. Figure 13 showed the relationship of the ozone conversion with the size of the GAC. With the smaller size, the frequency of contact between the GAC ozone was increasing, so the conversion of ozone decomposition was increasing.

Larger surface area was also associated with impurities. The smaller the size of the GAC, the impurities that covered the pore and the surface was less than the bigger size of GAC. Figure 13 also showed the CuO_x influence on ozone decomposition. With bigger loading of CuO_x, the conversion of ozone to oxygen increased because many ozone molecules were converted by CuO_x into oxygen molecules.

3.6. Catalyst Durability

CuO_x/GAC catalysts were tested for 8 hours. The results could be seen in figure 14.

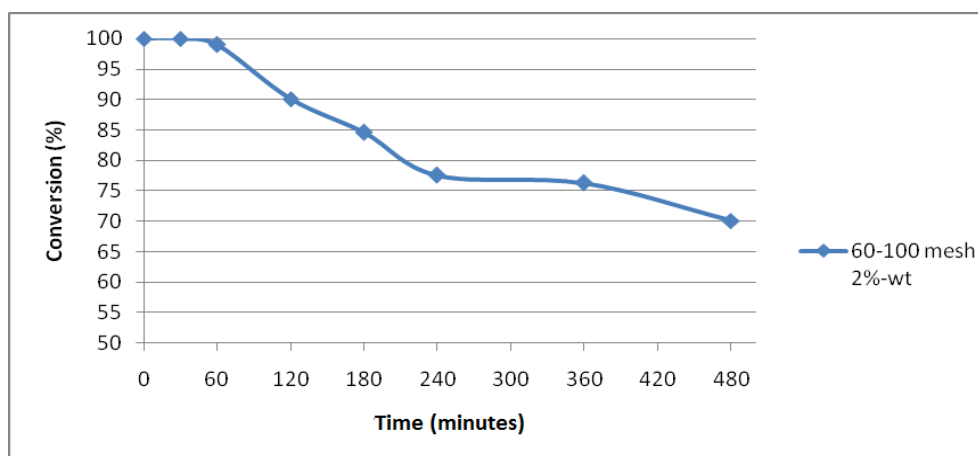


Figure 14. Average conversion of ozone decomposition of GAC.

CuO_x/GAC conversion decreased significantly 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. 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. Therefore, mask that contained CuO_x/GAC can be used to reduce the ozone concentration to be below the allowed threshold.

4. Conclusion

Decomposition of ozone can be done effectively using CuO_x catalyst with GAC as the support. CuO_x/GAC catalyst with size of 60-100 mesh and loading percentage of 2 %-wt have the highest conversion value being reached 100%. Size and loading percentage of the catalyst had a relationship with the conversion of ozone in which the smaller size of a catalyst based on CuO_x easily dispersed to the support and higher percentage of CuO_x could convert higher ozone to oxygen molecules. CuO_x/GAC 2%-w 60-100 mesh could convert ozone to oxygen with a minimum of 70% within 8 hours.

5. Acknowledgments

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6. References

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