

Article

# Catalytic Decomposition of N<sub>2</sub>O over Cu–Zn/ZnAl<sub>2</sub>O<sub>4</sub> Catalysts

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**Abstract:** The catalytic decomposition of N<sub>2</sub>O was investigated over Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts in the temperature range of 400–650 °C. Catalytic samples have been prepared by wet impregnation method. Prepared catalysts were characterized using several techniques like BET surface area, X-ray diffraction (XRD), and Scanning electron microscopy (SEM). The Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> showed higher catalytic performance along with long term stability during N<sub>2</sub>O decomposition. The Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts yielded 100% N<sub>2</sub>O conversion at 650 °C. The Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts are promising for decrease this strong greenhouse gas in the chemical industry.

**Keywords:** N<sub>2</sub>O decomposition; greenhouse gas; ZnAl<sub>2</sub>O<sub>4</sub>; heterogeneous catalysis

## 1. Introduction

Global warming is focus of intensive concern worldwide. Nitrous oxide (N<sub>2</sub>O) is an invisible, non-poisonous gas that has been identified as a potential contributor for ozone destruction in the stratosphere over the past decade and recognized as a rather strong greenhouse gas [1]. N<sub>2</sub>O has a lifetime of 114–130 years under atmospheric conditions, and its global warming potential (GWP) is approximately 310 times higher than that of carbon dioxide (CO<sub>2</sub>) [2]. Now, the concentration of N<sub>2</sub>O in the atmosphere is still rising. The emission of N<sub>2</sub>O comes from both natural sources and human contributions. Natural emissions include terrestrial, marine, and atmospheric sources. The anthropogenic sources include mainly the biological transformation of fertilizer's nitrogen into N<sub>2</sub>O (agriculture), biomass burning, combustion of fossil fuels, industrial activities, wastewater treatment, aquaculture and the use of solvents. The continuous increase of N<sub>2</sub>O concentration in the atmosphere is mainly due to human activities such as adipic acid production, nitric acid production, fuel and biomass combustion, etc. [3,4]. For these reasons, researchers have paid a great deal of attention to N<sub>2</sub>O because of its possible environmental impacts. There are many methods that can be used to reduce the emission concentration of N<sub>2</sub>O, such as selective catalytic reduction with hydrocarbons (HC-SCR), thermal decomposition, selective adsorption, and direct catalytic N<sub>2</sub>O decomposition into N<sub>2</sub> and O<sub>2</sub> [5]. Among various types of abatement technologies, direct catalytic decomposition is economical and does not produce CO<sub>2</sub>, and becomes one of the most attracting methods. The catalytic decomposition of N<sub>2</sub>O (up to 450 °C) provides an attractive solution for reducing N<sub>2</sub>O emissions in tail gas from chemical processes. It is the most qualified method to reduce N<sub>2</sub>O emissions because it does not require the addition of reducing agents, and it does not produce harmful by-products.

A large number of catalysts, such as pure oxides, noble metals, mixed oxides, and iron zeolites have been evaluated for N<sub>2</sub>O decomposition reaction [6–10]. Among them, noble-metal catalysts

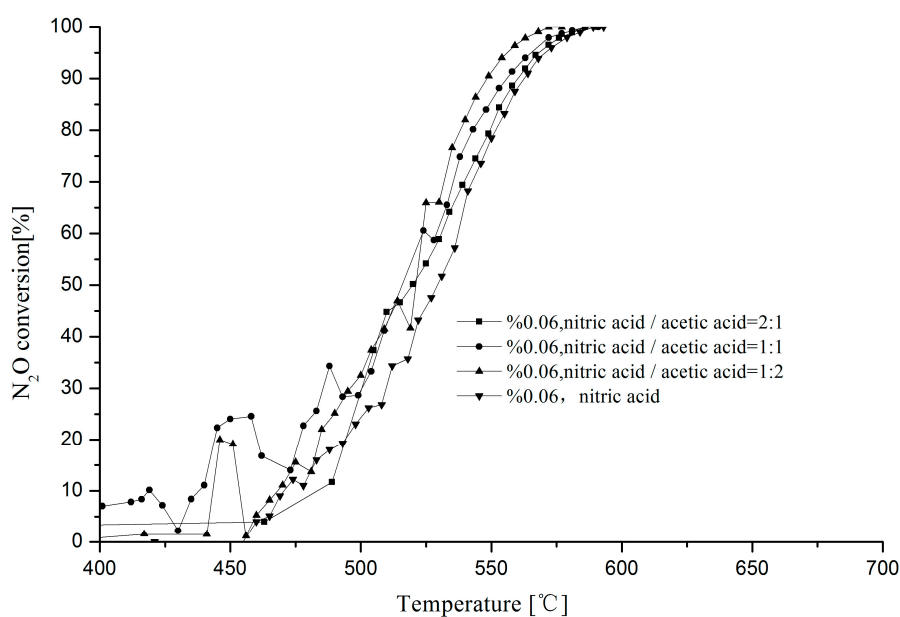
exhibit satisfactory activity at intermediate temperatures [11,12]. However, their high cost represents an important obstacle towards practical applications. Most zeolite-based catalysts can be largely deactivated in the presence of water vapor and excess oxygen and are very poor in practical applications. Considering lower economic cost and excellent catalytic performance, copper based materials has a great potential for industrial applications. It was reported that Cs-doped CuO,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Nd}_2\text{CuO}_4$  and Cu-containing zeolites were active for  $\text{N}_2\text{O}$  decomposition [13–16]. Zinc aluminate ( $\text{ZnAl}_2\text{O}_4$ ) has high mechanical resistance, high thermal stability, or inertness to water vapor, making it an attractive material for the catalyst and a carrier for active metals instead of the more traditional systems. High temperature calcination of  $\text{Al}_2\text{O}_3$ -supported metal nitrates is a convenient method to form spinel phase [17,18].

In this study, Cu-Zn/ $\text{ZnAl}_2\text{O}_4$  catalysts were prepared. Due to the use of cheap materials and simple preparation process, the manufacturing cost of Cu-Zn/ $\text{ZnAl}_2\text{O}_4$  catalysts is low. Their activity and stability for decomposition of  $\text{N}_2\text{O}$  are tested in the presence of oxygen. The expected results will be beneficial to industrial researchers in studying the catalytic decomposition of  $\text{N}_2\text{O}$ .

## 2. Results and Discussion

### 2.1. Effect of Mixed Acid Ratio on $\text{N}_2\text{O}$ Decomposition

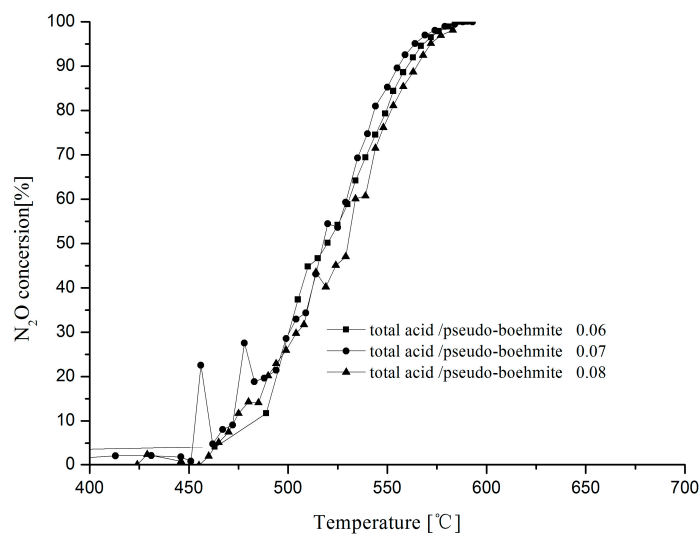
Figure 1 shows the effects of the different mixed acid ratio on the activity of Cu-Zn/ $\text{ZnAl}_2\text{O}_4$  in  $\text{N}_2\text{O}$  decomposition. It can be found that the use of inorganic and organic mixed acid solution as a solvent had certain effect on improving the catalytic activity of the catalyst. When the ratio of nitric acid to acetic acid was 1:2, the catalyst had a relatively high catalytic activity. Thus, the optimal ratio of nitric acid and acetic acid was 1:2 for preparing Cu-Zn/ $\text{ZnAl}_2\text{O}_4$ .



**Figure 1.** The catalytic activity for  $\text{N}_2\text{O}$  decomposition over the different mixed acid ratio catalysts.

### 2.2. Effect of Total Acid and Pseudo-Boehmite Ratio for $\text{N}_2\text{O}$ Decomposition

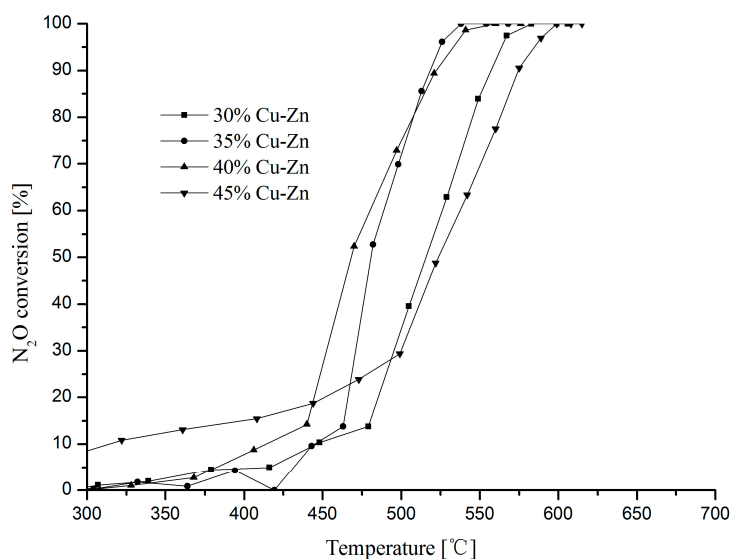
Figure 2 shows the  $\text{N}_2\text{O}$  decomposition performance over the different total acid and pseudo-boehmite ratio catalysts. It was clearly seen that under the same acetic acid and nitric acid ratio, the total acid and pseudo-boehmite ratio had little effect on the catalytic decomposition activity of the catalyst  $\text{N}_2\text{O}$ . Taking into account the economic reasons, the ratio of total acid and pseudo-boehmite was 0.06 that seemed appropriate for producing Cu-Zn/ $\text{ZnAl}_2\text{O}_4$ .



**Figure 2.** Effect of the different total acid and pseudo-boehmite ratio on the  $N_2O$  conversion.

### 2.3. Effect of Cu-Zn Loading Amount on $N_2O$ Decomposition

To investigate the effect of Cu-Zn loading amount on  $N_2O$  decomposition, several Cu-Zn/ $ZnAl_2O_4$  catalysts with different Cu-Zn loading amount were prepared. Figure 3 shows the catalytic performance results of  $N_2O$  decomposition over the Cu-Zn/ $ZnAl_2O_4$  with different Cu-Zn loading amount. As showed in Figure 3 below 450 °C, with the increase of Cu-Zn loading amount, the activity of the catalyst was gradually increased in the range of 30–45 wt %. Above 450 °C, addition of Cu-Zn loading amount increased the catalytic activity and then the activity decreased when Cu-Zn loading amount was increased to 45 wt %. The Cu-Zn loading amount has a more significant effect on catalytic activity above 450 °C. The result may suggest that suitable Cu-Zn loading amount is 35–40 wt %. It was recommended to use amount, which can save raw materials and reduce costs. Hence, this 35 wt % Cu-Zn loading amount was chosen as optimum for  $N_2O$  decomposition, and further studies were carried out using this Cu-Zn loading amount.



**Figure 3.** The effect of Cu-Zn loading amount on the decomposition of  $N_2O$ .

#### 2.4. Characterization of the Catalyst

The XRD patterns of the fresh Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> and used Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts are shown in Figures 4 and 5. Individual phases found in the samples were marked in the graph. The fresh and used catalyst exhibited a crystalline nature with dominating ZnAl<sub>2</sub>O<sub>4</sub> phase. In the XRD pattern of the fresh catalyst, ZnO phase (JCPDS Card No. 36-1451) was observed. The absence of any peaks belonging to the copper phase can be explained by considering the fact that the concentration of CuO particles was low and well dispersed on the surface of the catalyst. In the XRD pattern of the used catalyst, no diffraction peaks of ZnO were observed, most likely reason was the low concentration of ZnO after N<sub>2</sub>O decomposition reaction.

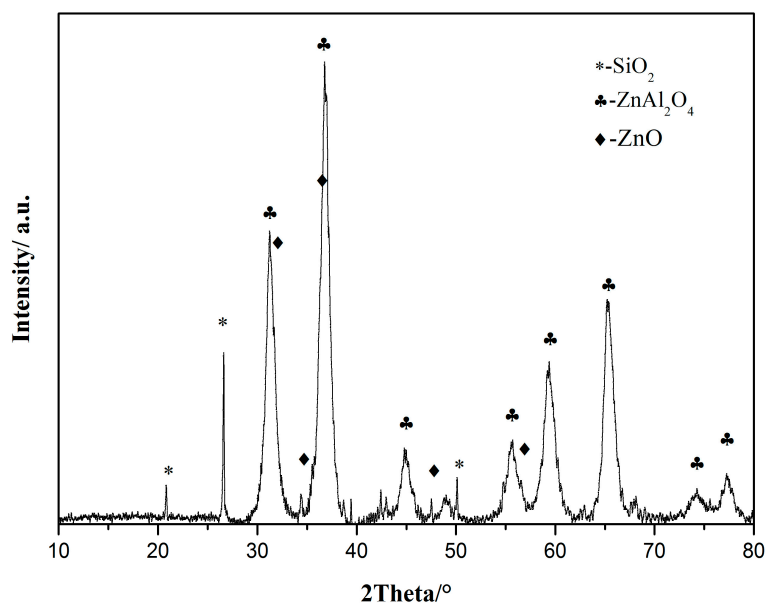


Figure 4. X-ray diffractogram of the fresh catalyst.

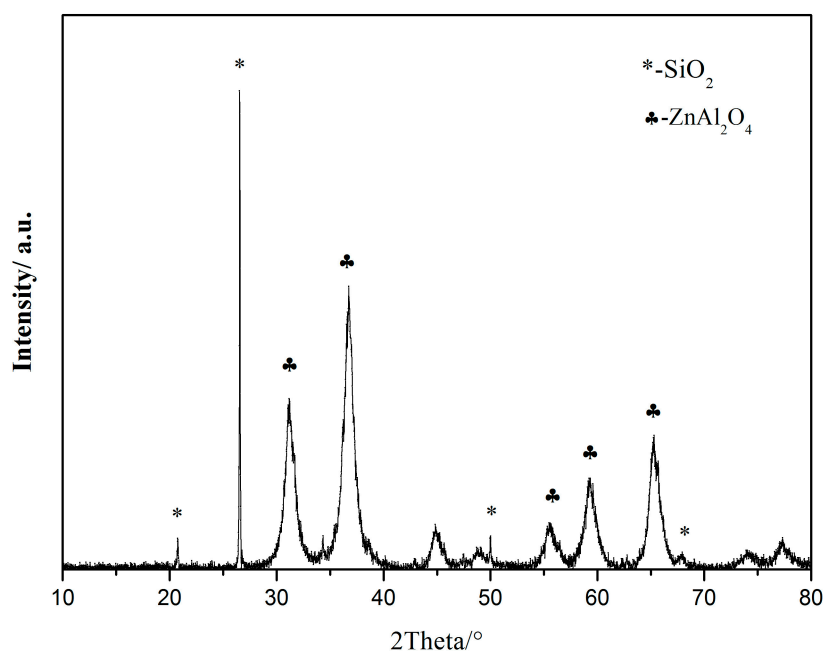


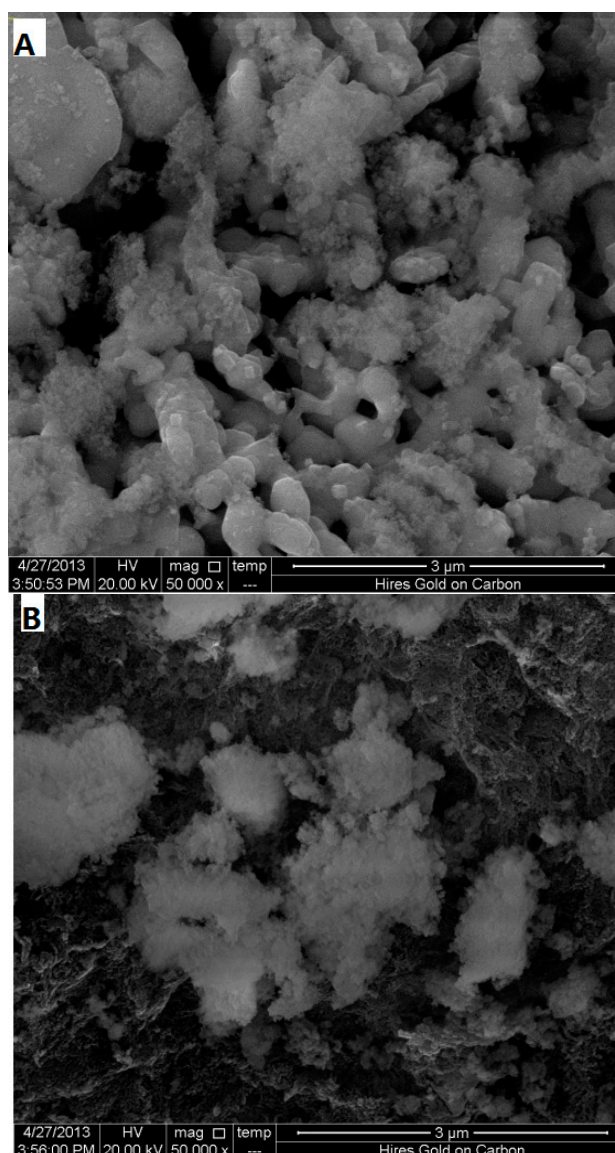
Figure 5. X-ray diffractogram of the used catalyst.

The BET specific surface area values of the fresh and used catalyst are reported in Table 1. As observed, the mean pore diameter of the used catalysts was lower than that of the fresh catalysts. However, the specific surface area of the used catalysts was larger than that of the fresh catalysts. The main cause of this change was that the porosity was developed after catalytic reaction. Furthermore, the surface areas ( $81.77\text{--}94.20\text{ m}^2\cdot\text{g}^{-1}$ ) obtained before and after the catalytic tests were not notably changed, indicating that the catalyst had good structural stability.

**Table 1.** BET area and pore diameter of the fresh and used catalyst.

Catalyst	BET Area ( $\text{m}^2\cdot\text{g}^{-1}$ )	Pore Diameter (nm)
fresh	81.77	77.0
used	94.20	75.4

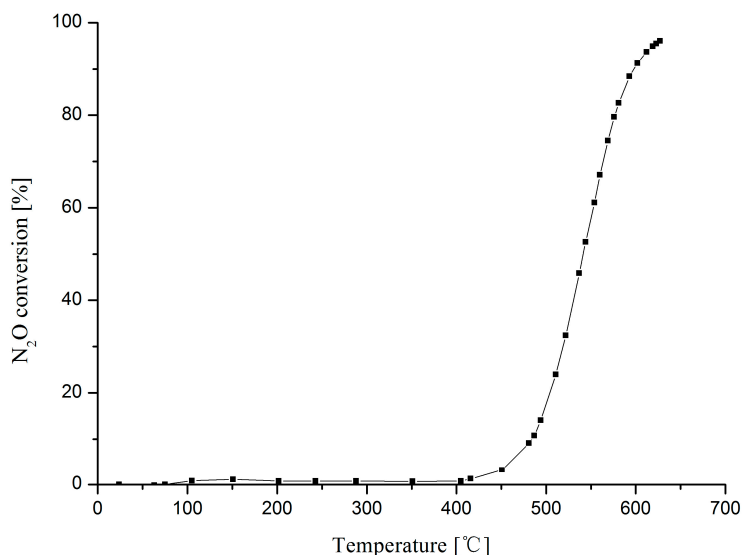
Figure 6 shows the surface morphology of the fresh and used catalyst. The fresh catalyst showed rough surface morphology with inhomogeneous small particles. The used catalyst had a low surface roughness, which was possibly due to gas flushing during the catalytic reaction.



**Figure 6.** SEM images of catalysts (A) the fresh catalyst and (B) the used catalyst.

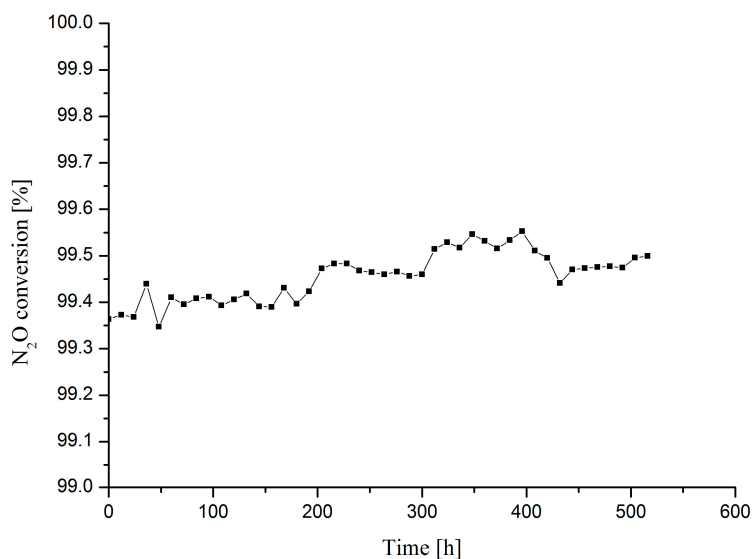
## 2.5. Catalytic Performance

The catalytic activity result for the Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts is presented in Figure 7. As shown in Figure 7, no obvious reaction was observed over the Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts until about 400 °C, and they started to show some activities above 450 °C. The temperature needs to be over 610 °C in order to reach 90% N<sub>2</sub>O conversion ( $T_{90}$ ).



**Figure 7.** Conversion of N<sub>2</sub>O over Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts. Reaction conditions: 8.1 vol % N<sub>2</sub>O, 10.2 vol % O<sub>2</sub>, N<sub>2</sub> balance, gas hourly space velocity (GHSV) = 1200 h<sup>-1</sup>.

The stability of catalysts is important in determining their practical usefulness. The catalytic stability of the Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalyst for N<sub>2</sub>O decomposition is shown in Figure 8. These tests were carried out at  $T = 650$  °C. In model atmosphere (8.1 vol % N<sub>2</sub>O, 10.2 vol % O<sub>2</sub>, N<sub>2</sub> balance), N<sub>2</sub>O conversion over the Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalyst after reaction at  $T = 650$  °C for 500 h keeps at 99%, indicating that the catalyst has high activity and stability.



**Figure 8.** Stability test run of the Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts at 650 °C for 500 h.



### 3. Experimental

#### 3.1. Supports Preparation

The supports used in this study were prepared by the kneading method. Pseudo-boehmite powder and  $\text{SiO}_2$  powder were thoroughly mixed with the inorganic binder, sesbania powder. Next, a mixed solution of nitric acid and acetic acid was added dropwise to the mixture in order to make slurry. The mixture was kneaded to best plastic state, then extruded, calcined at  $550\text{ }^\circ\text{C}$  for 4 h and shaped.

#### 3.2. Preparation of Cu-Zn/ $\text{ZnAl}_2\text{O}_4$ Catalysts

The supported Cu-Zn catalysts were prepared using an incipient wetness impregnation method. In a typical impregnation process,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and additives were dissolved in distilled water. The catalyst carrier was wetted with a small amount of water, and then the carrier was impregnated with the same volume in a mixed solution and kept at  $60\text{ }^\circ\text{C}$  for 24 h. After impregnation, each catalyst was dried in an oven at  $100\text{ }^\circ\text{C}$  for 10 h. The catalysts were then calcined at  $800\text{ }^\circ\text{C}$  for 6 h in air to obtain the Cu-Zn/ $\text{ZnAl}_2\text{O}_4$  catalysts. A photograph of prepared catalyst pellets is given in Figure 9. The catalyst is cylindrical granule with diameter of 5 mm and length of 5–10 mm.



Figure 9. A photograph of prepared catalyst pellets.

#### 3.3. Catalysts Characterization

BET surface area, pore diameter and pore volume of the catalysts were determined by  $\text{N}_2$  adsorption at  $-196\text{ }^\circ\text{C}$  using a Micrometrics ASAP 2020 instrument (ASAP2020, Micromeritics, Norcross, GA, USA). XRD patterns of the catalysts were recorded using an X-ray diffractometer (XRD-7000, Shimadzu, Kyoto, Japan) in with Cu  $\text{K}\alpha$  radiation. The  $2\theta$  range was kept between 10 and 80 degrees with a scan speed of  $6^\circ \cdot \text{min}^{-1}$ . Scanning electron microscope (SEM) (Quanta 400F, FEI Company, Hillsboro, OR, USA) was used to analyze the surface morphology of the catalyst.

#### 3.4. Activity Tests

The evaluation of catalysts for  $\text{N}_2\text{O}$  catalytic decomposition was carried out using a fixed-bed stainless steel reactor with an inner diameter of 58 mm and 850 mm in length. The catalyst bed

contained 60 mL of catalyst. The GHSV (gas hourly space velocity) was determined by dividing the standard gas flow rate by the catalyst bed volume. The reactant gas mixture (8.1 vol % N<sub>2</sub>O, 10.2 vol % O<sub>2</sub>, N<sub>2</sub> balance) was fed to the reactor. The composition simulates high concentration of N<sub>2</sub>O in the industrial process. The total flow rate was 1200 mL·min<sup>-1</sup>, which could be converted to a gas hourly space velocity (GHSV) of 1200 h<sup>-1</sup>. The reaction products were analyzed by using an on-line gas SP-3420 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

The N<sub>2</sub>O conversion was calculated according to the following equation:

$$X_{N_2O}(\%) = \frac{(C_{N_2O_{in}} - C_{N_2O_{out}})}{C_{N_2O_{in}}} \times 100 \quad (1)$$

where  $X_{N_2O}$  was the percent conversion of N<sub>2</sub>O;  $C_{N_2O_{in}}$  and  $C_{N_2O_{out}}$  were concentrations of N<sub>2</sub>O (ppm) in the inlet and outlet, respectively.

A long-term stability test was done at 650 °C and GHSV = 1200 h<sup>-1</sup>.

#### 4. Conclusions

In this work, Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts was prepared by high temperature calcination of Al<sub>2</sub>O<sub>3</sub>-supported metal nitrates and characterized by using XRD, SEM and N<sub>2</sub> adsorption-desorption. The Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalysts were used to reduce N<sub>2</sub>O emission of simulated sources based on their activity and stability tests. Prepared catalysts were tested for high concentration N<sub>2</sub>O catalytic decomposition. The results illustrate that Cu-Zn/ZnAl<sub>2</sub>O<sub>4</sub> catalyst is quite effective for the catalytic decomposition of N<sub>2</sub>O under model atmosphere. N<sub>2</sub>O can be completely decomposed at 650 °C in oxygen atmosphere. No deactivation and good performance of the catalyst were confirmed by 500 h stability tests.

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**Author Contributions:** Xiaoying Zheng and Runhu Zhang conceived and designed the experiments; Xiaoying Zheng performed the experiments; Fang Bai and Runhu Zhang analyzed the data; Chao Hua contributed reagents/materials/analysis tools; Runhu Zhang wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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