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# Catalytic N<sub>2</sub>O Decomposition over Cu/Mn/Zn Doped CeO<sub>2</sub> Composite Oxides

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**Abstract.** Cu/Mn/Zn oxides were firstly prepared by coprecipitation with molar ratio of Cu/Zn, 0.17, and Mn/(Cu+Zn) by 0.0~0.06, respectively. The temperature of N<sub>2</sub>O conversion ca. 10% over Cu/Zn and Cu/Mn<sub>0.03</sub>/Zn was 370°C and 325°C, respectively, by using 6.8(v)% N<sub>2</sub>O+balanced N<sub>2</sub>, and GHSV of 30000h<sup>-1</sup>, indicating the addition of manganese oxide could improve Cu/Zn oxide activity on N<sub>2</sub>O decomposition. The Cu/Mn/Zn doped CeO<sub>2</sub> composite oxides were further prepared with molar ratio of Ce/Cu by 0.0~1.4. The temperature of N<sub>2</sub>O conversion ca. 10% over Ce<sub>1.0</sub>/Cu/Mn<sub>0.03</sub>/Zn was 260°C as same conditions applied over Cu/Zn and Cu/Mn<sub>0.03</sub>/Zn samples. Stability test by using simulated mixture, 6.8(v)% N<sub>2</sub>O+5.0(v)% O<sub>2</sub>+3.0(v)% H<sub>2</sub>O+balanced N<sub>2</sub>, 580°C, GHSV of 30000h<sup>-1</sup>, showed that N<sub>2</sub>O conversion remained stable. Characterization demonstrated that the synergistic action of active components was the main origin of Ce<sub>1.0</sub>/Cu/Mn<sub>0.03</sub>/Zn sample had good performance on N<sub>2</sub>O abatement.

## 1. Introduction

It has been reported that N<sub>2</sub>O's global warming potential (GWP) would be about 300 times of CO<sub>2</sub>, and N<sub>2</sub>O also shows a long lifetime in the atmosphere. Moreover, its potential for depleting the stratospheric ozone layer is almost same as hydrochlorofluorocarbons (HCFCs), which has been considered as the most important ozone depleting substances (ODS) [1]. Among these technologies developed for N<sub>2</sub>O abatement potentially used in stationary and mobile processes, it is believed that the direct catalytic decomposition (DeN<sub>2</sub>O) approach is probably the most potential method due to its effectiveness and less energy requirements. Therefore, different kinds of materials have been widely reported for potentially applied in DeN<sub>2</sub>O system [2]. Catalysts based on the use of noble metals provide excellent performance for the catalytic decomposition of N<sub>2</sub>O at mild reaction temperatures, however, their performance is very sensitive to impurities contained in the waste gas such as H<sub>2</sub>O, O<sub>2</sub> as well as SO<sub>x</sub>, etc. [3]. Hong et al. [4] found that cerium-manganese composite oxides modified with alkali metal oxides, K<sub>2</sub>O, Na<sub>2</sub>O, etc., or alkaline earth metal oxides, CaO, BaO, etc., showed good activities and the best performance on N<sub>2</sub>O abatement was obtained by a Ba/Ce-Mn catalyst. Zhang et al. [5] used K<sub>2</sub>O or Na<sub>2</sub>O, etc., to modify zinc-magnesium-cobalt composite oxides and found that the catalyst activity for N<sub>2</sub>O decomposition was improved. Grzybek et al. [6] studies indicated (Co, Zn)Co<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>/cordierite catalyst gave good performance for N<sub>2</sub>O decomposition with the help of dispersion of zinc-cobalt-cerium composite compounds on the cordierite. Zabilskiy et al. [7] investigated series of copper-cerium composite oxides activity on N<sub>2</sub>O decomposition and indicated that the best N<sub>2</sub>O decomposition activity was obtained over the sample ca. 10% content of copper.



However, the catalyst activity was found to be deteriorative in the presence of small amounts of O<sub>2</sub> and H<sub>2</sub>O, etc., in waste gas mixture [8].

This paper provided a preliminary report on catalytic N<sub>2</sub>O decomposition over Cu/Mn/Zn doped CeO<sub>2</sub> composite oxides prepared by coprecipitation method as well as typical characterization results.

## 2. Experimental

### 2.1. Sample preparation

The high dispersive samples used in this study were synthesized by coprecipitation method. A prepared basic solution was dripped to the solution with suitable amounts of manganese nitrate, zinc nitrate, cupric nitrate or cerous nitrate (CP grade, China), and the resulted precipitate was aged overnight, and then filtered, washed by using distilled water till the filtrate pH reached *ca.* 7.0, and dried at 105 °C overnight, followed by calcination in a muffle furnace for 3h at 550 °C in static air. The prepared samples were referred as Cu/Mn<sub>x</sub>/Zn, x-indicating the molar ratio of Mn/Cu-Zn, and Ce<sub>y</sub>/Cu/Mn<sub>x</sub>/Zn, y-indicating the molar ratio of Ce/Cu, respectively.

### 2.2. Characterization

X-ray diffractometry (XRD) was performed by using a computerized Rigaku D/max-RB diffractometer (Japan, CuK $\alpha$  radiation,  $\lambda=0.154\text{nm}$ , 50kV, 40mA). H<sub>2</sub>-TPR was performed on a fully automated instrument (AutoChem II 2920 Micromeritics, USA).

### 2.3. Evaluation on catalyst activity

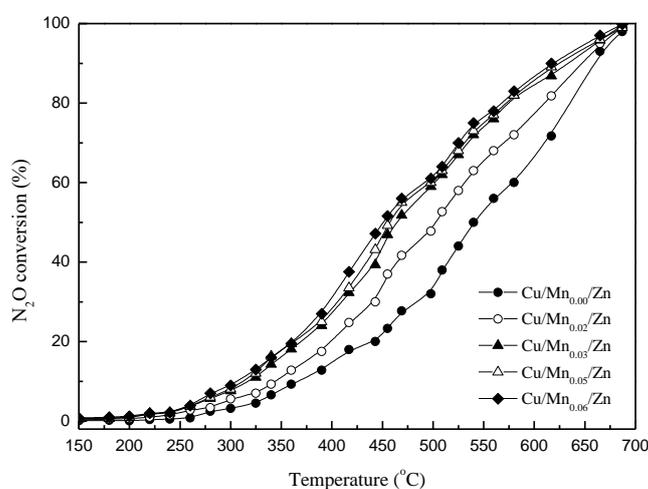
N<sub>2</sub>O abatement was investigated in a laboratory micro reactor. The mixture compositions of both in- and out-reactor were detected by using an on-line gas chromatograph (GC-2010 PLUS, Shimadzu, Japan) equipped with HP-PLOT/Q capillary columns and an ECD detector, respectively. The sample activity was shown as N<sub>2</sub>O conversion under used experimental conditions, which was obtained with respect to the concentrations of N<sub>2</sub>O from inlet and outlet of the reaction system.

## 3. Results and discussion

### 3.1. Activity over Cu/Mn<sub>x</sub>/Zn catalysts

The activity tests indicated N<sub>2</sub>O decomposition over Cu/Mn<sub>x</sub>/Zn composite oxides has been improved with the addition of manganese oxide to the sample at the following used conditions, hourly space velocity of 30000h<sup>-1</sup>, and the mixture of 6.8(v)% N<sub>2</sub>O+balanced N<sub>2</sub>. However, it showed that the activity over Cu/Mn<sub>x</sub>/Zn composite oxides was not obviously increased when the molar ratio of Mn/Cu-Zn was reached to 0.03, *i.e.* the sample of Cu/Mn<sub>0.03</sub>/Zn, under used experimental conditions (Figure 1).

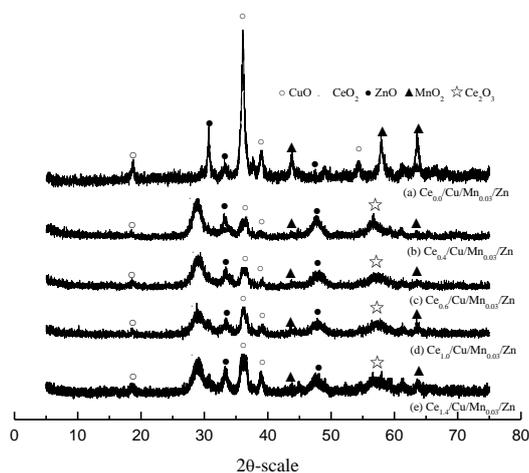
Stability test also showed that the Cu/Mn<sub>0.03</sub>/Zn sample gave good performance under applied experimental conditions, while its activity was degraded when the feed stream contained some amounts of O<sub>2</sub> and water vapor. The following researches by improving copper-manganese-zinc composite oxides performance on N<sub>2</sub>O decomposition were referred to the compositions of Cu/Mn<sub>0.03</sub>/Zn catalyst.



**Figure 1.** The influence of manganese oxide on  $N_2O$  conversion over  $Cu/Mn_x/Zn$  samples

### 3.2. $Ce_y/Cu/Mn_{0.03}/Zn$ performance on $N_2O$ decomposition

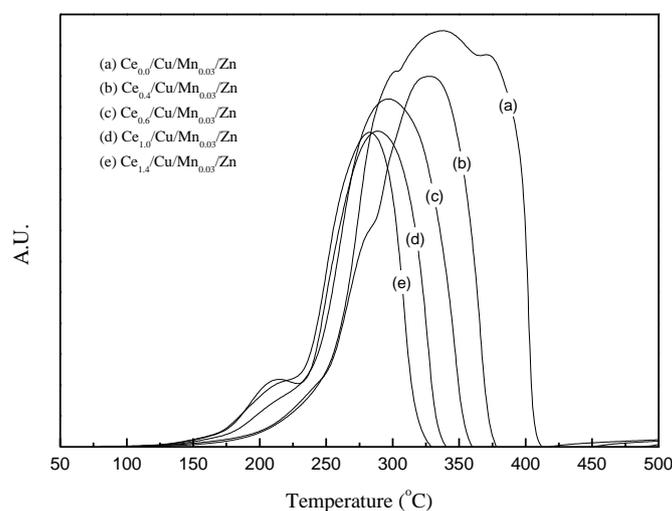
**3.2.1. Characterization.** Figure 2 depicted XRD spectra over samples prepared with different  $Ce/Cu$  molar ratios, respectively. It indicated that the characterized XRD peaks of  $CuO$  and  $MnO_2$  appearing in  $Ce_y/Cu/Mn_{0.03}/Zn$  composite oxides were gradually reduced by increasing the molar ratio of  $Ce/Cu$  on samples. This could be probably the main factor that the surface area of  $Ce_y/Cu/Mn_{0.03}/Zn$  composite oxides was slightly increased by doping cerium oxide to  $Cu/Mn_{0.03}/Zn$  composite oxide.



**Figure 2.** XRD patterns over  $Ce_y/Cu/Mn_{0.03}/Zn$  composite oxides

$H_2$ -TPR experiments were also performed over  $Ce_y/Cu/Mn_{0.03}/Zn$  composite oxides and results have been depicted in Figure 3. It was found that the sample of copper-manganese-zinc composite oxide showed a wide reduction peak within the temperature from *ca.* 200°C to 400°C, which was corresponding to reduction of the oxide species on sample surface, and two shoulder characterized peaks also shown at *ca.* 360°C and 385°C in TPR profile, which could be ascribed to the reduction of Cu oxide and Mn oxide, respectively. It was interesting that the doping cerium oxide to  $Cu/Mn_{0.03}/Zn$  composite oxide resulted in a downward shift at  $H_2$ -TPR profiles, which implied that by doping

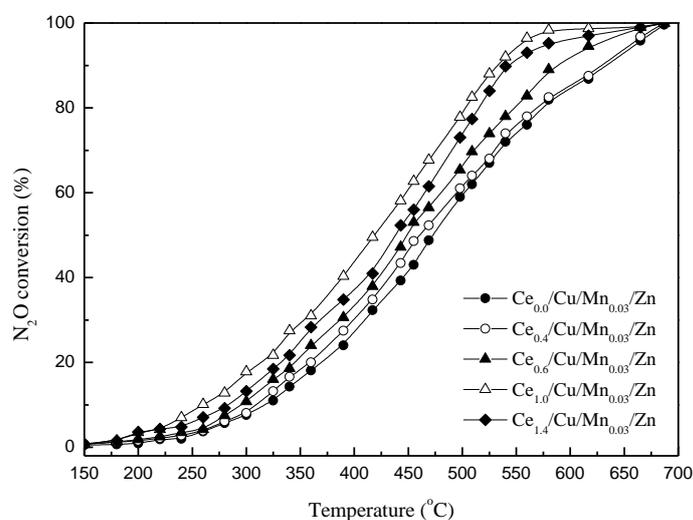
cerium oxide to  $\text{Cu/Mn}_{0.03}/\text{Zn}$  composite oxide could improve its reducibility with respect to cupric oxide on samples.



**Figure 3.**  $\text{H}_2$ -TPR profiles over  $\text{Ce}_y/\text{Cu/Mn}_{0.03}/\text{Zn}$  composite oxides

**3.2.2.  $\text{N}_2\text{O}$  decomposition over  $\text{Ce}_y/\text{Cu/Mn}_{0.03}/\text{Zn}$  samples.** The activity results showed that  $\text{N}_2\text{O}$  abatement over  $\text{Ce}_y/\text{Cu/Mn}_{0.03}/\text{Zn}$  composite oxides was improved by doping cerium oxide to  $\text{Cu/Mn}_{0.03}/\text{Zn}$  composite oxide under following applied conditions, hourly space velocity of  $30000\text{h}^{-1}$ , and mixture of 6.8(v)%  $\text{N}_2\text{O}$ +balanced  $\text{N}_2$ , respectively (Figure 4). The order on  $\text{N}_2\text{O}$  decomposition was  $\text{Ce}_{1.0}/\text{Cu/Mn}_{0.03}/\text{Zn} > \text{Ce}_{1.4}/\text{Cu/Mn}_{0.03}/\text{Zn} > \text{Ce}_{0.6}/\text{Cu/Mn}_{0.03}/\text{Zn} > \text{Ce}_{0.4}/\text{Cu/Mn}_{0.03}/\text{Zn} > \text{Ce}_{0.0}/\text{Cu/Mn}_{0.03}/\text{Zn}$  under tested conditions. More detailed studies were carried out by using the sample of  $\text{Ce}_{1.0}/\text{Cu/Mn}_{0.03}/\text{Zn}$ . It was found that small amounts of  $\text{O}_2$  or  $\text{H}_2\text{O}$  existing in the feed only slightly inhibited the catalyst's  $\text{N}_2\text{O}$  decomposition performance. This could be because the coprecipitation method ensured sufficient dispersion of active components and enhanced the synergistic interaction among the active components and thus alleviated the effect of  $\text{O}_2$  or  $\text{H}_2\text{O}$  on catalytic  $\text{N}_2\text{O}$  conversion.

Stability test was carried out over  $\text{Ce}_{1.0}/\text{Cu/Mn}_{0.03}/\text{Zn}$  catalyst to evaluate its potential performance for  $\text{N}_2\text{O}$  abatement in practical application (data not shown). Result showed that  $\text{N}_2\text{O}$  conversion (ca. 95%) almost kept stable lasted for 100h under the following used experimental conditions, reaction temperature of  $580^\circ\text{C}$ , simulated gas mixture of 6.8(v)%  $\text{N}_2\text{O}$ +5.0(v)%  $\text{O}_2$ +3.0(v)%  $\text{H}_2\text{O}$ +balanced  $\text{N}_2$ , and GHSV of  $30000\text{h}^{-1}$ , respectively.



**Figure 4.** The effect of cerium content on  $N_2O$  abatement over  $Ce_y/Cu/Mn_{0.03}/Zn$  composite oxides

#### 4. Conclusions

$H_2$ -TPR characterization over  $Ce_y/Cu/Mn_{0.03}/Zn$  composite oxides showed that by doping cerium oxide to  $Cu/Mn_{0.03}/Zn$  composite oxide was benefit for the reduction of active components as well as leading to the increasing in samples surface area. Structural characterization (XRD) over  $Ce_y/Cu/Mn_{0.03}/Zn$  samples prepared by coprecipitation method showed that by doping cerium oxide to  $Cu/Mn_{0.03}/Zn$  composite oxide was beneficial for the active components well dispersed on the sample, indicating the synergistic action of catalytic components was the main origin that  $Ce_{1.0}/Cu/Mn_{0.03}/Zn$  catalyst showed good activity and stability on  $N_2O$  abatement when using a more practical simulated feed with  $N_2O$  in  $N_2$  rather than in Ar as well as containing amounts of  $O_2$  and  $H_2O$ , respectively.

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