

# Catalytic decomposition of N<sub>2</sub>O over Co-Ce mixed oxide catalyst

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## Abstract

A series of CoCeO<sub>x</sub> catalysts with different ratios of Ce/Co were prepared by the hydrothermal method and their activities for the decomposition of N<sub>2</sub>O have been investigated. It was found that CoO-CeO<sub>2</sub> mixed oxide catalyst showed higher activity than pure Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub>. The co-existence of Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> exhibited a synergetic effect, which inhibited the crystallization of the Co<sub>3</sub>O<sub>4</sub> phase, leading to the high surface area. More importantly, the redox property of CoO-CeO<sub>2</sub> mixed oxide is also improved due to the interaction between Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub>. As a result, CoCeO<sub>x</sub> catalyst exhibited high activity for the decomposition of N<sub>2</sub>O.

**Keywords:** Nitrous oxide; Co-Ce mixed oxide catalyst; Catalytic decomposition

## 1. Introduction

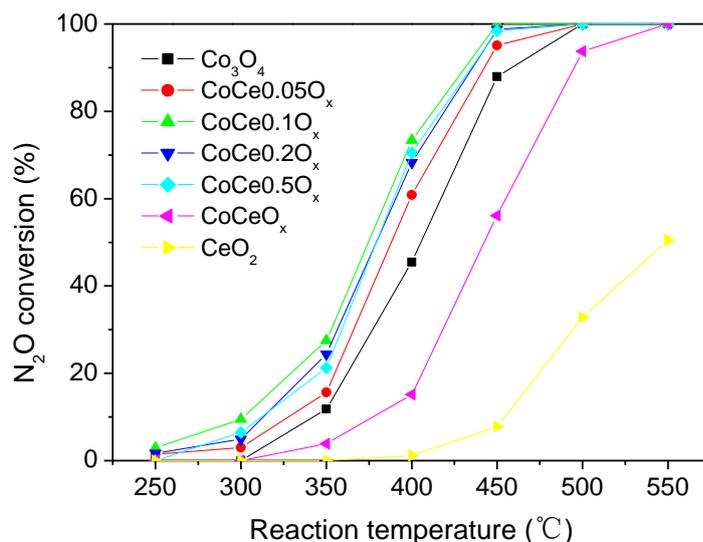
Nitrous oxide (N<sub>2</sub>O) is not only one of the most powerful greenhouse gases, but also cause the destruction of the stratospheric ozone layer (Ravishankara *et al.*, 2009). Therefore, the removal of N<sub>2</sub>O has attracted more and more attention and different methods have been employed for the control of N<sub>2</sub>O. Among the different methods developed the catalytic decomposition is regarded as the most promising choice due to its high efficiency and the low costs (Konsolakis *et al.*, 2015). Noble metals, such as Rh and Ru, are active for the decomposition of N<sub>2</sub>O (Liu *et al.*, 2016). However, the high cost of noble metal has

limited their practical applications. Recently, many researchers have focused on the development of metal oxide catalyst for the catalytic decomposition of N<sub>2</sub>O due to the low cost. Among the metal oxides, CuO, NiO and Co<sub>3</sub>O<sub>4</sub> (Zhou *et al.*, 2012) showed relatively high activities for the decomposition of N<sub>2</sub>O. In viewpoint of practical application, the activities of these catalysts need to be improved. CeO<sub>2</sub> has been reported to be a promoter of metal oxide due to the high oxygen storage-release capacity via Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycle. Cu<sub>x</sub>Ce<sub>1-x</sub>O<sub>y</sub> mixed oxide catalysts were found to be more active than the pristine CuO and CeO<sub>2</sub> catalysts, and Cu<sub>0.67</sub>Ce<sub>0.33</sub>O<sub>y</sub> exhibited the highest activity among the Cu-Ce mixed oxides with different Cu/Ce molar ratios (Zhou *et al.*, 2012). CeO<sub>2</sub> supported Co<sub>3</sub>O<sub>4</sub> catalyst was also more active than CeO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> catalysts (Grzybek *et al.*, 2016). Previous research showed that the preparation method exerted a significant effect on the activity of the catalyst (Konsolakis *et al.*, 2015). To date, Co-Ce mixed oxide prepared by the hydrothermal method has seldom been reported for the N<sub>2</sub>O decomposition. The objective of the current work is to develop the Co-Ce mixed oxide catalyst via the hydrothermal method. It was found that Co-Ce mixed oxide catalyst showed higher activity than the pristine CoO and CeO<sub>2</sub>. Based on the catalyst characterization, the relationship between the structure of the catalyst and the catalytic activity has been elucidated.

**Table 1.** BET surface area of the different catalysts.

Catalyst	BET surface area (m <sup>2</sup> /g)
Co <sub>3</sub> O <sub>4</sub>	68
CoCe0.05O <sub>x</sub>	108
CoCe0.1O <sub>x</sub>	115
CoCe0.2O <sub>x</sub>	112
CoCe0.5O <sub>x</sub>	107
CoCeO <sub>x</sub>	79
CeO <sub>2</sub>	63





**Figure 1.** N<sub>2</sub>O conversion as a function of reaction temperature over Co<sub>3</sub>O<sub>4</sub>, CeO<sub>2</sub> and Co-Ce mixed oxide catalysts. Conditions: [N<sub>2</sub>O]=2000ppm, [O<sub>2</sub>]=2%, GHSV=38,000 h<sup>-1</sup>.

## 2. Experimental

### 2.1. Catalyst preparation

Co-Ce mixed oxides with different molar ratios of Co/Ce were prepared by the hydrothermal method. The resulting powder was dried at 120°C overnight and then calcined in air at 500 °C. The obtained mixed oxide is denoted by CoCe<sub>x</sub>O<sub>y</sub>, where *x* represents the molar ratio of Ce/Co. For comparison, pristine Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> catalysts were also prepared by the same preparation method.

### 2.2. Activity tests

The activity tests for N<sub>2</sub>O decomposition were performed in a fixed-bed quartz reactor using a 0.2 g catalyst of 40-60 mesh. N<sub>2</sub>O decomposition was tested in the temperature range of 250-550 °C. The reactant mixture consisted of 2000 ppm N<sub>2</sub>O, 0 or 2% O<sub>2</sub> and helium as the balance gas. The total flow rate of the feed gas was 200 cm<sup>3</sup>·min<sup>-1</sup>, corresponding to a GHSV of 38,000 h<sup>-1</sup>. The composition of the gas in the inlet and outlet streams was analyzed by a gas chromatograph (Shimadzu GC 2014 equipped with Porapak Q).

### 2.3. Catalyst characterization

Surface area of the catalysts was evaluated from N<sub>2</sub> adsorption at 77 K by the BET method on a Quantachrome Autosorb AS-1 system. Powder X-ray diffraction (XRD) pattern was obtained on a Bruker D8 ADVANCE diffractometer using Cu K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg K $\alpha$  radiation, calibrated internally by carbon deposit C 1s binding energy (BE) of 284.8 eV. Temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were conducted on a chemisorption analyzer

## 3. Results and discussions

### 3.1. Comparison of the activity

The catalytic activity of Co<sub>3</sub>O<sub>4</sub>, CeO<sub>2</sub> and Co-Ce mixed oxide catalysts for the decomposition N<sub>2</sub>O in the presence of oxygen is illustrated in Fig. 1. Pure CeO<sub>2</sub> showed poor activity. Co<sub>3</sub>O<sub>4</sub> exhibited relatively high activity. It is evident that the addition of some amount of Ce to Co<sub>3</sub>O<sub>4</sub>(CoCe0.05O<sub>x</sub>) showed a noticeable promoting effect. With the ratio of Ce/Co increasing from 0.05 to 0.1, NO<sub>x</sub> conversion was further increased. However, with further increasing of the molar ratio of Ce/Co, the activity began to decrease. It is evident that CoCe0.10O<sub>x</sub> catalyst showed the highest activity, which is noticeably higher than that of Co<sub>3</sub>O<sub>4</sub>. This fact indicates that the introduction of appropriated Ce to Co leads to the enhanced activity for the decomposition of N<sub>2</sub>O.

### 3.2. N<sub>2</sub>-adsorption, XRD and H<sub>2</sub>-TPR

The BET surface areas of the studied catalysts are presented in Table 1. Compared with Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub>, Co-Ce mixed oxide catalyst possessed higher surface area. The high surface area would contribute to the high catalytic performance. Based on the XRD analysis it was found that over Co-Ce mixed oxide catalyst both Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> phase are present. The interaction between Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> leads to the smaller particle size of the catalyst. H<sub>2</sub>-TPR results showed that the synergetic effect between Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub> resulted in the enhancement of the redox property, which is very important for decomposition of N<sub>2</sub>O.

## 4. Conclusions

Compared with  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$ , Co-Ce mixed oxide exhibited higher activity for the decomposition of  $\text{N}_2\text{O}$  in the presence of oxygen, and the optimum molar ratio of Ce/Co is 0.1. The high catalytic activity of Co-Ce mixed oxide was ascribed to the synergetic effect between  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$ . The strong interaction between  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$  not only leads to high surface area but also promotes the redox property, both of which contribute to the activity enhancement.

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