

Catalytic decomposition of N₂O over Co-Ce mixed oxide catalyst

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Abstract

A series of CoCeO_x catalysts with different ratios of Ce/Co were prepared by the hydrothermal method and their activities for the decomposition of N₂O have been investigated. It was found that CoO-CeO₂ mixed oxide catalyst showed higher activity than pure Co₃O₄ and CeO₂. The co-existence of Co₃O₄ and CeO₂ exhibited a synergetic effect, which inhibited the crystallization of the Co₃O₄ phase, leading to the high surface area. More importantly, the redox property of CoO-CeO₂ mixed oxide is also improved due to the interaction between Co₃O₄ and CeO₂. As a result, CoCeO_x catalyst exhibited high activity for the decomposition of N₂O.

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

1. Introduction

Nitrous oxide (N₂O) 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 N₂O has attracted more and more attention and different methods have been employed for the control of N₂O. 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 N₂O (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 N₂O due to the low cost. Among the metal oxides, CuO, NiO and Co₃O₄ (Zhou *et al.*, 2012) showed relatively high activities for the decomposition of N₂O. In viewpoint of practical application, the activities of these catalysts need to be improved. CeO₂ has been reported to be a promoter of metal oxide due to the high oxygen storage-release capacity via Ce⁴⁺/Ce³⁺ redox cycle. Cu_xCe_{1-x}O_y mixed oxide catalysts were found to be more active than the pristine CuO and CeO₂ catalysts, and Cu_{0.67}Ce_{0.33}O_y exhibited the highest activity among the Cu-Ce mixed oxides with different Cu/Ce molar ratios (Zhou *et al.*, 2012). CeO₂ supported Co₃O₄ catalyst was also more active than CeO₂ and Co₃O₄ 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 N₂O 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 CeO₂. 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 ² /g)
Co ₃ O ₄	68
CoCe0.05O _x	108
CoCe0.1O _x	115
CoCe0.2O _x	112
CoCe0.5O _x	107
CoCeO _x	79
CeO ₂	63

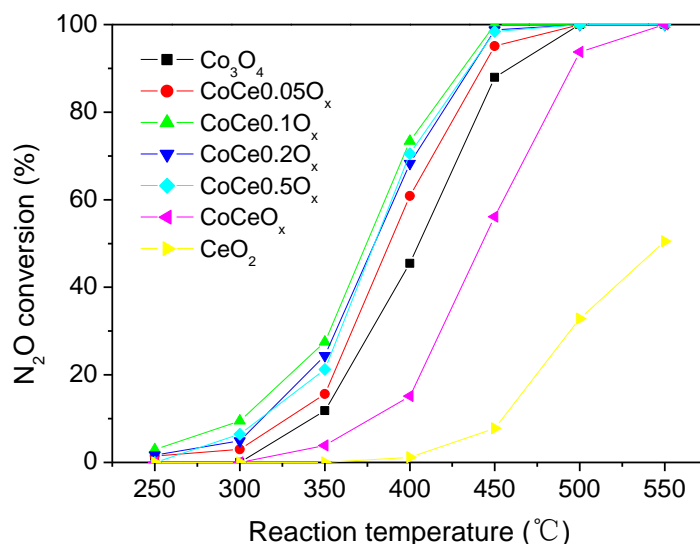


Figure 1. N₂O conversion as a function of reaction temperature over Co₃O₄, CeO₂ and Co-Ce mixed oxide catalysts. Conditions: [N₂O]=2000ppm, [O₂]=2%, GHSV=38,000 h⁻¹.

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_xO_y, where *x* represents the molar ratio of Ce/Co. For comparison, pristine Co₃O₄ and CeO₂ catalysts were also prepared by the same preparation method.

2.2. Activity tests

The activity tests for N₂O decomposition were performed in a fixed-bed quartz reactor using a 0.2 g catalyst of 40-60 mesh. N₂O decomposition was tested in the temperature range of 250-550 °C. The reactant mixture consisted of 2000 ppm N₂O, 0 or 2% O₂ and helium as the balance gas. The total flow rate of the feed gas was 200 cm³·min⁻¹, corresponding to a GHSV of 38,000 h⁻¹. 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 N₂ 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 α radiation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg K α radiation, calibrated internally by carbon deposit C 1s binding energy (BE) of 284.8 eV. Temperature-programmed reduction (H₂-TPR) experiments were conducted on a chemisorption analyzer

3. Results and discussions

3.1. Comparison of the activity

The catalytic activity of Co₃O₄, CeO₂ and Co-Ce mixed oxide catalysts for the decomposition N₂O in the presence of oxygen is illustrated in Fig. 1. Pure CeO₂ showed poor activity. Co₃O₄ exhibited relatively high activity. It is evident that the addition of some amount of Ce to Co₃O₄(CoCe0.05O_x) showed a noticeable promoting effect. With the ratio of Ce/Co increasing from 0.05 to 0.1, NO_x 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_x catalyst showed the highest activity, which is noticeably higher than that of Co₃O₄. This fact indicates that the introduction of appropriated Ce to Co leads to the enhanced activity for the decomposition of N₂O.

3.2. N₂-adsorption, XRD and H₂-TPR

The BET surface areas of the studied catalysts are presented in Table 1. Compared with Co₃O₄ and CeO₂, 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 Co₃O₄ and CeO₂ phase are present. The interaction between Co₃O₄ and CeO₂ leads to the smaller particle size of the catalyst. H₂-TPR results showed that the synergetic effect between Co₃O₄ and CeO₂ resulted in the enhancement of the redox property, which is very important for decomposition of N₂O.

4. Conclusions

Compared with Co_3O_4 and CeO_2 , Co-Ce mixed oxide exhibited higher activity for the decomposition of N_2O 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 Co_3O_4 and CeO_2 . The strong interaction between Co_3O_4 and 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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