Improvement of N_2O decomposition activity over N_2O-pretreatment Ce*x*Co catalysts: the effects of deposited oxygen species from N_2O dissociation

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Abstract: In this work, obvious improvement of N_2O catalytic decomposition activity over Ce-Co-O mixed oxides catalysts was observed. The fresh and N_2O-pretreatment catalysts were tested under specific conditions and characterized by Raman, XPS, H_2-TPR, TPD studies. It was found the doped CeO_2 stored more deposited oxygen species (O*) from N_2O dissociation, facilitating another surface-to-N_2O electron transfer route (from deposited O* to N_2O) leading to the cleavage of N-O bond. N_2O pretreatment at higher temperature resulted in more deposited O*, which accounts for the enhancement of decomposition activity over N_2O-pretreatment Ce-Co-O catalysts.

Keywords: N_2O catalytic decomposition, Ce-Co-O mixed oxides, Oxygen species from N_2O dissociation.

1. Introduction

The direct catalytic decomposition of N_2O is the most promising technology to draw down N_2O emissions [1,2]. The Ce-doped cobalt spinel catalyst showed outstanding catalytic performance with good tolerance to H_2O and O_2 [3]. In our studies, an obvious enhancement of N_2O decomposition activity over N_2O-pretreatment Ce-doped cobalt spinel catalyst was observed unexpectedly. And our conclusion might be generally adoptable to other Ce-doped catalysts and zeolites catalysts.

2. Experimental

The Co_3O_4 and Ce-Co-O mixed oxides (abbreviated as Ce*x*Co, where *x* represented the mol% of Ce) were prepared by co-precipitation method. The steady-state reaction conditions were as follows: 1000 ppm N_2O, He balanced, 300 ml/min gas flow rate, 0.2 g catalyst, GHSV of 80000 h^{-1}. The pretreatment of N_2O was conducted at 500 °C for 1 h at the same conditions of steady-state reaction. XPS analysis was performed on an electron spectrometer (ESCALab220i-XL, VG Scientific). H_2-TPR profiles were recorded on a ChemiSorb 2720 TPx chemisorption analyzer in 10% H_2/Ar (30 mL/min) atmosphere.

3. Results and discussion

Fig. 1 showed that the decomposition activity of post-pretreatment Ce*x*Co catalysts was obviously enhanced, T_{90} of Ce10Co catalyst decreased from 359 to 312 °C. But hardly any enhancement was observed for Co_3O_4. A trend that the enhancement of decomposition activity was positively related to the doping amount of CeO_2 was concluded.

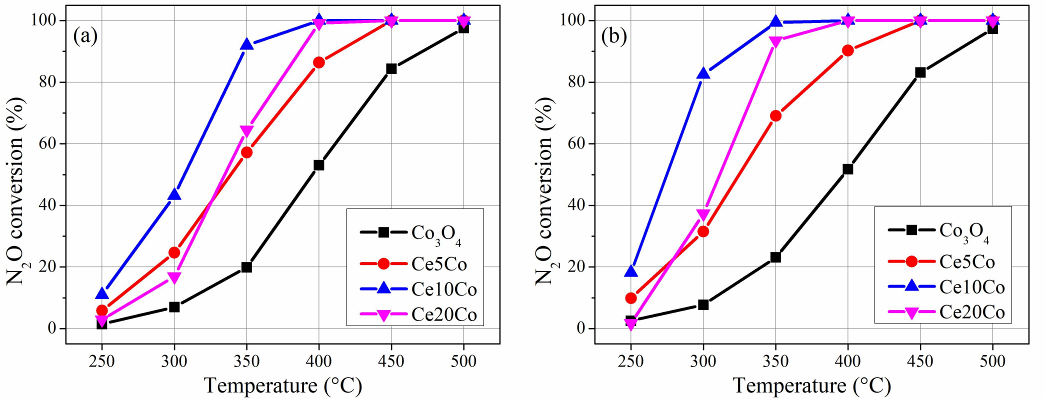

Figure 1. N_2O decomposition activity of Ce*x*Co and Co_3O_4 catalysts, (a) fresh catalysts; (b) N_2O-pretreatment catalysts.

As shown in Fig 2(a), the band at around 531.0 and 529.7 eV could be ascribed to surface adsorbed oxygen species (O_α) and lattice oxygen (O_β), respectively [4]. After N_2O pretreatment, the relative content of O_α over Co_3O_4 changed little. But the relative content of O_α over Ce10Co increased from 48.8% to 53.6%. It suggested that N_2O pretreatment would deposit specific adsorbed oxygen species on Ce10Co and the doping of CeO_2 helped store more such oxygen species. The catalytic decomposition of N_2O could be described by the following reaction [1,2].

$$N_2O + * \rightarrow N_2 + O* \tag{1}$$

$$O* + O* \Leftrightarrow O_2 + 2* \tag{2}$$

$$N_2O + O* \rightarrow N_2 + O_2 + * \tag{3}$$

The removal of surface adsorbed oxygen species (O*) from N_2O dissociation is commonly recognized as the rate-determining step. In the initial stage of catalytic decomposition of N_2O, reaction 1 is faster than reaction 2 due to the abundant active sites. Hence, the deposited oxygen species detected by XPS generated from the dissociation of N_2O. The reduction peak below 200 °C in Fig. 2(b) is able to characterize deposited oxygen species (O*) [5]. It was clear that the peak area increased significantly after N_2O pretreatment, which was due to the accumulation of O*. H_2-TPR results further revealed that the doping of CeO_2 could offer more storage capacity for deposited O*.

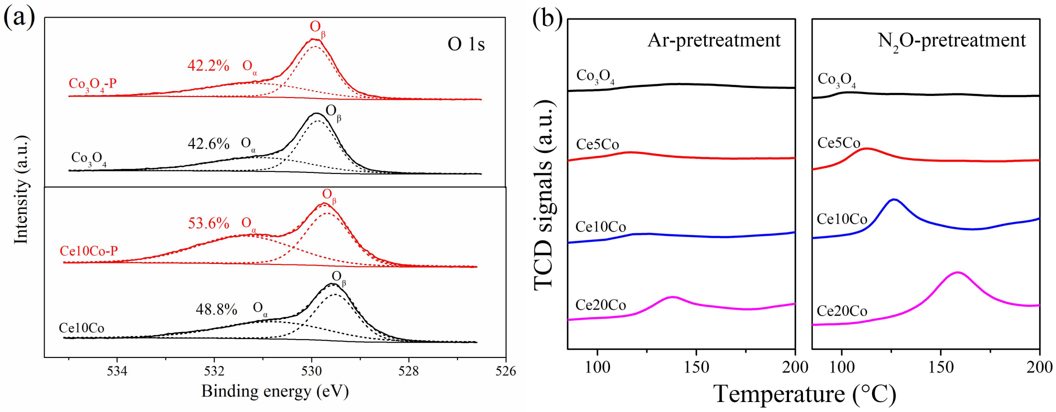

Figure 2. (a) O 1s XPS spectra of fresh, N_2O-pretreatment Co_3O_4 and Ce10Co catalysts; (b) H_2-TPR profiles (below 200 °C) of Ar-pretreatment and N_2O-pretreatment Ce*x*Co catalysts.

It was also proved that pretreatment at higher temperature would lead to more formation of deposited O*. After being cooled down to lower temperature, there are still massive O* remained on the surface. The remaining O* availed surface-to-N_2O electron transfer route (from deposited O* to N_2O) leading to N_2O dissociation (reaction 3), thus promoting the N_2O decomposition activity. In addition, the long-term test showed that the deposited O* would be consumed completely in a dozen hours at 350 °C.

4. Conclusions

The doping of CeO_2 improved the N_2O decomposition activity and oxygen storage capacity of Co_3O_4. Surface adsorbed oxygen species (O*) generated from the dissociation of N_2O would deposit on the surface of Ce*x*Co. With the accumulation of O*, the reaction of O* with gaseous N_2O would occur substantially over Ce*x*Co. Pretreatment of N_2O at higher temperature results in more deposited O*, which accounts for the enhancement of decomposition activity over N_2O-pretreatment Ce*x*Co.

References

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