



# Selective catalytic oxidation of ammonia to nitrogen over ceria–zirconia mixed oxides

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## ABSTRACT

The selective catalytic oxidation of ammonia to nitrogen ( $\text{NH}_3$ -SCO) has been studied over ceria–zirconia mixed oxides ( $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ). The addition of Zr into ceria led to the phase transition from the cubic fluorite structure to the tetragonal structure and the generation of oxygen vacancies. The  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  ( $0.2 \leq x \leq 0.8$ ) mixed oxide catalysts exhibited certain amount of moderate acid sites. Particularly, the  $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$  catalyst achieved the largest amount of moderate acid sites and highest proportion of  $\text{Ce}^{3+}$  (oxygen vacancies). Meanwhile, it showed the best  $\text{NH}_3$  oxidation activity, and the complete conversion temperature was about  $360^\circ\text{C}$ . In addition, numerical results also indicated that the higher zirconium content in  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  catalysts improved the  $\text{N}_2$  selectivity which was about 100% with  $x > 0.4$ . The formation of  $\text{N}_2\text{O}$  was the main reason for low  $\text{N}_2$  selectivity over these catalysts ( $x \leq 0.4$ ) proved by TPSR experiments. Meanwhile, the reaction mechanism of  $\text{NH}_3$  with lattice oxygen was observed to be different from the gaseous oxygen, and the gaseous oxygen species was much more active than lattice oxygen for  $\text{NH}_3$  oxidation.

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## 1. Introduction

The treatment of ammonia from waste streams is becoming an important issue due to ever increasing environmental concerns. It is known that there are a lot of chemical processes that use ammonia as a reactant or produce ammonia as a by-product. They all act as potential sources of  $\text{NH}_3$  slips [1]. Thus, the removal of ammonia from waste streams is becoming an increasingly important issue. In order to control the ammonia slip, several reviews of different techniques used for the elimination of ammonia have been published, such as adsorption, absorption, chemical treatment, catalytic decomposition, and selective catalytic oxidation (SCO) [2]. Selective catalytic oxidation of ammonia to nitrogen is potentially an ideal technology for removing ammonia from oxygen-containing waste gases, and consequently it is of increasing interest in recent years [1–11].

So far, a variety of studies have been conducted to seek efficient catalysts with low cost and enhanced catalytic capability for  $\text{NH}_3$  oxidation. Several types of material, such as noble metal (Ag, Pt, Pd, Ru, Ir) [2,4,6,12], transition metal oxides ( $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{MoO}_3$ , NiO) [3,6,10,13,14], and rare earth or mixed oxides ( $\text{CeO}_2$ , Mg–Al–O) [15,16], have been developed for SCO of ammonia. Usually noble metal catalysts show superior catalytic performance at

relatively low temperatures ( $200$ – $350^\circ\text{C}$ ). However, the selectivity for  $\text{N}_2$  on these catalysts are relatively low (typically  $\leq 80\%$ ). Transition metal oxides and mixed oxides catalysts with low cost exhibit higher  $\text{N}_2$  selectivity, but the operation temperature is significantly higher ( $300$ – $400^\circ\text{C}$ ).

Cerium oxide was well known to have a high oxygen exchange capacity, which was related to the capacity of cerium to change oxidation states reversibly between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  by receiving or giving up oxygen [17]. Ceria ( $\text{CeO}_2$ ) was thus rendered a very effective catalyst to operate the reaction that involved oxygen. Lou et al. have reported that  $\sim 99.2\%$   $\text{NH}_3$  conversion was achieved during catalytic oxidation over Cu–Ce (6:4, molar/molar) catalyst at  $400^\circ\text{C}$  and the overall selectivity of  $\text{N}_2$  production varied from 19% to 82% [15]. However, pure ceria would result in a significant efficiency decrease under thermally harsh environment. Therefore, a new generation of mixed oxides containing  $\text{CeO}_2$  and  $\text{ZrO}_2$  has been developed. The ceria–zirconia mixed oxides have been applied in a number of different fields, for example, as active supports, “oxygen buffers” in the three-way catalysis elimination of CO,  $\text{NO}_x$  and hydrocarbons, water–gas shift reaction, and so forth. Compared with pure ceria, in the ceria–zirconia mixed oxides,  $\text{Ce}^{4+}$  was partially substituted for  $\text{Zr}^{4+}$  in the lattice of  $\text{CeO}_2$ . Hori et al. [18] found that the beneficial effects of  $\text{ZrO}_2$  were pronounced in  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  catalysts of which oxygen storage capacity was three to five times higher than that of the pure  $\text{CeO}_2$ . Moreover, the doping effect of zirconium can maintain the reversible  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox property even after exposure to the reduction condition above  $900^\circ\text{C}$

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