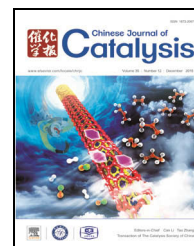


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## Article

# Relationship between oxygen species and activity/stability in heteroatom (Zr, Y)-doped cerium-based catalysts for catalytic decomposition of CH<sub>3</sub>SH



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## ABSTRACT

CeO<sub>2</sub>, Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>, and Ce<sub>1-x</sub>Y<sub>x</sub>O<sub>2-δ</sub> (x = 0.25, 0.50, 0.75, and 1.00) have been rapidly synthesized to estimate their catalytic behavior in decomposing CH<sub>3</sub>SH. The role of oxygen vacancies, and the relationship between the oxygen species and catalytic properties of CeO<sub>2</sub> and Zr-doped and Y-doped ceria-based materials are investigated in detail. Combining the observed catalytic performance with the characterization results, it can be deemed that surface lattice oxygen plays a critical role in methanethiol catalytic conversion over cerium oxides. Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> shows higher catalytic activity for CH<sub>3</sub>SH decomposition due to the large amount of surface lattice oxygen, readily available oxygen species, and excellent redox properties. Ce<sub>0.75</sub>Y<sub>0.25</sub>O<sub>2-δ</sub> displays better catalytic stability owing to the greater number of oxygen vacancies that would promote bulk lattice oxygen migration to the surface of the catalyst in order to replenish surface lattice oxygen. In addition, the results show that the difference in chemical valence between Ce and the heteroatoms would strongly influence the amount of surface lattice oxygen as well as the mobility of bulk-phase oxygen in these catalysts, thus affecting their activity and stability.

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## 1. Introduction

Methanethiol, a volatile organic compound (VOC) existing in petroleum gas, natural gas etc., has been reported to cause serious human health and environmental problems when it is emitted into the atmosphere [1,2]. Therefore, the mercaptan content in these fossil fuels should be decreased to the lowest level (1–5 ppmv) [3] in the petroleum refining industry. Besides, CH<sub>3</sub>SH is unacceptable because it can lead to emissions of

SO<sub>x</sub> and severe corrosion of metals, which is unfavorable for the transportation, storage, and use of these petroleum products [4–7]. Accordingly, eliminating CH<sub>3</sub>SH from natural gas and petroleum gas is urgently needed for the production of clean fossil fuels. Among all the methods for removing CH<sub>3</sub>SH [8–13], catalytic decomposition has been recognized as an efficient, economic, and ecological method; moreover, this method does not require additional reagents (O<sub>2</sub>, H<sub>2</sub>, etc.), and it produces only a small amount of pollutants [8,9].

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Cerium oxide or ceria, due to its prominent capability of oxygen storage/release, has been extensively applied to many catalytic reactions, including three-way catalytic converters (TWC) [14,15], hydrocarbon dry and steam reforming [16,17], fuel cell technology [18], low-temperature water gas shift [19,20], and deep oxidation of VOCs [21–23]. The oxygen storage/release ability of ceria can be attributed to the cyclic switch between  $Ce^{4+}$  and  $Ce^{3+}$  oxidation states ( $CeO_2 \leftrightarrow CeO_{2-x} + 1/2x O_2$ ) [24,25].

Of late, the application of ceria-based materials as catalysts to decompose  $CH_3SH$  has also attracted much attention due to the production of simple and tractable inorganic products [26–31]. Laosiripojana and coworkers studied the decomposition behavior of  $CH_3SH$  over a  $CeO_2$  catalyst for the first time and found that  $CH_3SH$  could be completely decomposed to simple and tractable carbon products ( $CH_4$ ,  $CO$ , and  $CO_2$ ) and sulfur products ( $H_2S$  etc.) [26]. However, the drawback of the catalyst was the high conversion temperature; the corresponding temperature for the complete catalytic conversion of  $CH_3SH$  reached 800 °C. In our previous study, it was found that  $CH_3SH$  can be completely decomposed at 450 °C over  $CeO_2$  nanoparticles with a large surface area [28,29]. Unfortunately, nanoscale  $CeO_2$  catalysts are usually deactivated within 10 h in time-on-stream tests. A series of rare-earth (RE, RE = Gd, Nd, Sm, etc.) modified cerium-based catalysts were developed to exhibit stability during the catalytic decomposition of  $CH_3SH$ , as compared to  $CeO_2$  [30,31]. The results indicate that the improved stability of the RE-doped catalysts is related to the formation of more oxygen vacancies; however, the role of oxygen vacancies in promoting catalytic stability has not been expounded. More importantly, the deactivation mechanism of  $CH_3SH$  over ceria-based catalysts, and the interrelation between the oxygen species and catalytic behavior is not well understood. Therefore, it is necessary to further investigate the contribution of oxygen vacancies in improving the catalytic stability as well as reveal the relationship between the catalytic behavior and oxygen species.

In order to realize these objectives, we chose dopants with different valences (trivalent and tetravalent) and ionic radii as compared to Ce and studied the effects of valence and ionic radius of ceria dopants in the doped ceria-based catalysts on their activity and stability during  $CH_3SH$  decomposition. We know that yttrium-doped ceria-based materials exhibit the best catalytic stability for  $CH_3SH$  conversion among a series of trivalent ion (RE, RE =  $Y^{3+}$ ,  $Gd^{3+}$ ,  $Sm^{3+}$ ,  $La^{3+}$ , and  $Nd^{3+}$ )-doped ceria-based catalysts [30,31]. Moreover, the radius of the  $Y^{3+}$  ion (1.03 Å) is greater than that of the  $Ce^{4+}$  ion (0.97 Å). Therefore, the  $Y^{3+}$  ion was chosen as the trivalent dopant. Besides, it is widely accepted that the incorporation of  $Zr^{4+}$  increases the surface area, oxygen storage capability, and thermal stability, leading to outstanding catalytic ability [32–34]. As far as we know, there are no previous studies on  $Zr^{4+}$ -doped cerium-based oxides for  $CH_3SH$  conversion. Meanwhile,  $Zr^{4+}$  (0.84 Å) has a smaller ionic radius than does  $Ce^{4+}$  (0.97 Å). Therefore, Zr was specifically chosen as the tetravalent dopant. Based on the above considerations, it can be deduced that Zr and Y ions are suitable for doping with ceria.

In this study,  $CeO_2$  and a series of heteroatom-doped Ce-based catalysts ( $Ce_{1-x}Zr_xO_2$  and  $Ce_{1-x}Y_xO_{2-\delta}$ ,  $x = 0.25, 0.50, 0.75, \text{ and } 1.00$ ) were prepared by a citric acid complexation method with the aid of microwaves to research the impact of the valence and ionic radius on their catalytic activity and stability for  $CH_3SH$  decomposition. The aim of this study is to investigate the role of oxygen vacancies, and the relationship between oxygen species and catalytic behavior via a series of characterization techniques. The aforesaid relationship can be classified into two categories: (1) relationship between surface lattice oxygen and catalytic activity and (2) relationship between bulk lattice oxygen migration and catalytic stability. Exploration of these two types of relationship will contribute to understanding the connection between the inherent properties of cerium-based materials and their catalytic behavior, and provide a fundamental basis for developing more efficient ceria-based catalysts.

## 2. Experimental

### 2.1. Sample preparation

The major procedures to rapidly prepare a series of  $Ce_{1-x}Zr_xO_2$  and  $Ce_{1-x}Y_xO_{2-\delta}$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ) solid solutions and  $CeO_2$ ,  $ZrO_2$ , and  $Y_2O_3$  catalysts by a citric acid complexation method using microwaves include the following steps. Calculated quantities of  $Ce(NO_3)_3 \cdot 6H_2O$ ,  $Zr(NO_3)_4 \cdot 5H_2O$ ,  $Y(NO_3)_3 \cdot 6H_2O$ , and citric acid were added to deionized water [28], and the mixed solution was continuously stirred for 5 min in a water bath at 60 °C until it became transparent. This solution was then calcined at 600 °C in air for 4 h using a microwave muffle furnace (CEM Business Enterprise, America, phoenix standard unit).

### 2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-1200 diffractometer (Cu  $K_\alpha$  irradiation), operating at 30 mA and 40 kV. The diffraction patterns were recorded in the  $2\theta$  range of 20° to 80° with a step size of 0.02°. The crystal phases were ascertained using the software of MDI Jade 5.0 and the particle size was calculated from the main diffraction peaks using the Scherrer formula. Further, the lattice constant “ $a$ ” was calculated using the principal diffraction peak (111) based on the following equation [35]:

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (1)$$

$$d = \frac{\lambda}{2 \sin \theta} \quad (2)$$

here,  $d$  is the inter-planar spacing and  $\theta$  corresponds to the angle of the diffraction peak (111).

$N_2$  adsorption-desorption isotherms were recorded on an automatic adsorption instrument (ASAP2020) at -196 °C. Prior to analysis, the sample was degassed under high vacuum at 300 °C for 2 h. The specific surface of the samples was calculated using the Brunauer-Emmett-Teller (BET) method.

The X-ray photoelectron spectra (XPS) of the samples were

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