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Article

Relationship between oxygen species and activity/stability in heteroatom (Zr, Y)-doped cerium-based catalysts for catalytic decomposition of CH₃SH

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ABSTRACT

CeO₂, Ce_{1-x}Zr_xO₂, and Ce_{1-x}Y_xO_{2-δ} ($x = 0.25, 0.50, 0.75$, and 1.00) have been rapidly synthesized to estimate their catalytic behavior in decomposing CH₃SH. The role of oxygen vacancies, and the relationship between the oxygen species and catalytic properties of CeO₂ 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_{0.75}Zr_{0.25}O₂ shows higher catalytic activity for CH₃SH decomposition due to the large amount of surface lattice oxygen, readily available oxygen species, and excellent redox properties. Ce_{0.75}Y_{0.25}O_{2-δ} 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, CH₃SH is unacceptable because it can lead to emissions of

SO_x and severe corrosion of metals, which is unfavorable for the transportation, storage, and use of these petroleum products [4–7]. Accordingly, eliminating CH₃SH from natural gas and petroleum gas is urgently needed for the production of clean fossil fuels. Among all the methods for removing CH₃SH [8–13], catalytic decomposition has been recognized as an efficient, economic, and ecological method; moreover, this method does not require additional reagents (O₂, H₂, 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 ($\text{CeO}_2 \leftrightarrow \text{CeO}_{2-x} + 1/2x \text{O}_2$) [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 ($\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, $x = 0.25, 0.50, 0.75$, 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 $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ ($x = 0.25, 0.50$, 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 $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ / $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 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 ($\text{Cu K}\alpha$ irradiation), operating at 30 mA and 40 kV. The diffraction patterns were recorded in the 2θ 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 θ 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

generated with a monochromatic Al- K_{α} excitation spectrometer. The carbon C-H photopeak at 284.6 eV was used for correcting the binding energies.

The Raman spectra were collected on a Via Reflex Raman spectrometer with a refrigerated CCD detector using an Ar⁺ laser with a 514 nm emission line at room temperature.

The redox behavior of the catalysts was analyzed by temperature programmed reduction (TPR) using a thermal conductivity detector (TCD) in order to measure the consumption of H₂. The catalyst sample (50 mg) was pretreated by calcination in 5% O₂/Ar for 60 min at 400 °C, after which it was cooled to 100 °C in Ar. Lastly, the temperature was increased to 900 °C at a ramp rate of 10 °C/min in a 10% H₂/Ar flow.

The oxygen storage capacity (OSC) of the Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Y_{0.25}O_{2-δ} samples was also evaluated by CO pulse injection using a microreactor system. Before measurement, 50 mg of the sample was firstly treated in a flow of 20% O₂/He (30 mL/min) for 1 h at 500 °C. Later, this material was cooled down to 450 °C in a He flow. A pulse of pure CO gas was introduced for 10 s every 6 min through a six-port valve with a measuring ring (50 μmol) at 450 °C. Ten sequences of CO pulses were employed in 1 h. The total OSC (TOSC) was calculated by summing the OSC of 10 CO pulses, which was indicated as μmol of [O] per gram of catalyst (μmol [O]/g).

2.3. Catalytic behavior evaluation

The catalytic behavior of the samples during CH₃SH decomposition was analyzed at atmospheric pressure in a home-made tubular fixed-bed reactor. The catalyst samples (0.2 g) with a particle size of 0.25–0.42 mm were loaded into

the quartz reactor. The CH₃SH decomposition reaction was conducted using a feed gas of 1% CH₃SH/N₂ at 30 mL/min. The concentration of CH₃SH in the gas stream was evaluated using a two GC gas chromatograph with two flame ionization detectors (FIDs), one thermal conductivity detector (TCD), and one flame photometric detector (FPD).

3. Results and discussion

3.1. Crystal structure and textural properties

3.1.1. XRD

The XRD patterns of Ce_{1-x}Zr_xO₂, Ce_{1-x}Y_xO_{2-δ} ($x = 0.25, 0.50, 0.75$, and 1.00), and CeO₂ are shown in Fig. 1. The pattern of CeO₂ matched well with the reference pattern (PDF 34-0394), which is an indication of the cubic fluorite-like structure of CaF₂ [36]. As for the Ce_{1-x}Zr_xO₂ and Ce_{1-x}Y_xO_{2-δ} samples ($x = 0.25, 0.50$, and 0.75), the diffraction peaks indexed to the reflections of (111), (200), (220), (331), (222), (400), (331), and (420) planes were observed, thus implying that the typical fluorite-like cubic structure is well maintained after being doped with heteroatoms (Zr and Y). Moreover, it could be seen that no phases assigned to Zr and Y species were detected in the patterns of Ce_{1-x}Zr_xO₂ or Ce_{1-x}Y_xO_{2-δ}. This phenomenon may be due to the following two reasons. Both Zr and Y entered into the lattice of CeO₂, forming homogeneous solid solutions [37]. Second, some Zr or Y species were highly dispersed with very small crystallites and/or presented an amorphous structure, much below the XRD detection limit [38,39]. In addition, the diffraction peak intensities of Ce_{1-x}Zr_xO₂ and Ce_{1-x}Y_xO_{2-δ} were slightly weaker than those of CeO₂, which may be related to the

Fig. 1. (A) XRD patterns of CeO₂ (a), Ce_{0.75}Zr_{0.25}O₂ (b), Ce_{0.5}Zr_{0.5}O₂ (c), Ce_{0.25}Zr_{0.75}O₂ (d), and ZrO₂ (e). (B) XRD patterns of CeO₂ (a), Ce_{0.75}Y_{0.25}O_{2-δ} (b), Ce_{0.5}Y_{0.5}O_{2-δ} (c), Ce_{0.25}Y_{0.75}O_{2-δ} (d), and Y₂O₃ (e).

insertion of Zr and Y cations into the lattice of CeO_2 . According to Fig. 1 (inset), the diffraction peak belonging to $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ gradually shifted towards larger 2θ values with increasing Zr loading, as shown in Fig. 1(A), whereas the corresponding diffraction of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ shifted to smaller 2θ values. These differences in the diffraction angles (2θ) of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ are closely associated with the fact that the radius of the Zr^{4+} ion (0.84 Å) is lesser than that of the Ce^{4+} ion (0.97 Å), but the radius of Y^{3+} (1.03 Å) is slightly larger than that of the Ce^{4+} ion. The insertion of Zr^{4+} with its smaller radius into the ceria unit cell will cause lattice contraction, whereas the incorporation of Y^{3+} with its larger radius into the CeO_2 unit cell will lead to lattice expansion. The corresponding lattice parameters and crystallite sizes of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0.25, 0.50, 0.75$, and 1.00), and CeO_2 are shown in Table 1. Obviously, the lattice parameters of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (5.348 Å), $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$ (5.274 Å), and $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ (5.195 Å) were smaller, while the parameters of $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ (5.410 Å), $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$ (5.407 Å), and $\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$ (5.403 Å) were larger than that of CeO_2 (5.400 Å). Besides, the diffraction peaks of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ were wider than that of CeO_2 , which indicates that the crystallite sizes of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ are smaller than that of CeO_2 , which in turn is due to the inserted heteroatoms effectively suppressing the growth of crystallites. According to the results calculated using the Scherrer equation, the corresponding crystallite sizes of CeO_2 , $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$, $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$, $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$, and $\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$ were 12.0, 7.1, 6.8, 7.6, 7.5, 5.9, and 4.5 nm, respectively, as shown in Table 1.

From the above-described XRD results, we can conclude that Zr and Y cations are inserted into the ceria lattice. However, it is not clear whether separate Zr and Y species with small crystallites or amorphous structures are formed on the surface of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$.

3.1.2. XPS

Table 1

The specific surface areas, crystallite sizes, and lattice parameters of the oxide solid solutions, $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$.

Oxide composition	Surface area ^a (m ² /g)	Crystallite size ^b (nm)	Lattice parameter "a"
CeO_2	42.8	12.0	5.400
$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	57.4	7.1	5.348
$\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$	35.3	6.8	5.274
$\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$	30.2	7.6	5.195
ZrO_2	6.9	14.5	5.111
$\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$	50.71	7.5	5.410
$\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$	31.9	5.9	5.407
$\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$	21.9	4.5	5.403
Y_2O_3	11.6	13.6	5.316

^a Determined by BET.

^b Determined by MDI Jade 5.0 and the Scherrer equation.

To demonstrate that separate Zr and Y species do not exist on the surface of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, XPS was used to characterize ZrO_2 , $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$, $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$, Y_2O_3 , $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$, and $\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$ to evaluate the composition and chemical state on their surfaces. Zr 3d XPS spectra of ZrO_2 , $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$, and $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ are shown in Fig. 2(A), while Y 3d XPS spectra of Y_2O_3 , $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$, and $\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$ are shown in Fig. 2(B). It is clear that both the Zr 3d and Y 3d XPS spectra could be deconvoluted with two peaks, which are associated with the contribution of two spin-orbit components. As shown in Fig. 2(A), two photoelectron peaks of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$, and $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ originated from the contributions of Zr 3d_{3/2} and Zr 3d_{5/2}, which were located at 181.8 and 184.2 eV, respectively. The photoelectron peaks centered at 156.7 and 158.8 eV have been attributed to Y 3d_{5/2} and Y 3d_{3/2} [40], respectively. It could be seen in Table 2 that the relative contents of Zr in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$, and $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ were 25.9, 51.8, and 75.4 wt%, respectively; meanwhile, the

Fig. 2. (A) Zr 3d XPS spectra of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (a), $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$ (b), $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ (c), and ZrO_2 (d). (B) Y 3d XPS spectra of $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ (a), $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$ (b), $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ (c), and Y_2O_3 (d).

Table 2Relative contents of Zr and Y in the $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ samples.

Sample	Relative content of Zr ^a (%)	Sample	Relative content of Y ^b (%)
$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	25.9	$\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$	24.4
$\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$	51.8	$\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$	52.6
$\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$	75.4	$\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$	76.2
ZrO_2	100.0	Y_2O_3	100.0

^a Calculated by the ratio of the total area of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ to ZrO_2 in the Zr 3d region.The areas were calculated according to the following equation, $A_{\text{Zr}} = A(\text{Zr } 3d_{5/2}) + A(\text{Zr } 3d_{3/2})$, using a CasaXPS processing program.^b Calculated by the ratio of the total area of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ to Y_2O_3 in the Y 3d region.The areas were calculated according to the following equation, $A_{\text{Y}} = A(\text{Y } 3d_{5/2}) + A(\text{Y } 3d_{3/2})$, using a CasaXPS processing program.

corresponding Y content in $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$, and $\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$ were 24.4, 52.6, and 76.2 wt%, respectively, which are almost consistent with the theoretically calculated values (25, 50, and 75 wt%, respectively). Combining with the results of XRD characterization (Fig. 1), which indicate that the diffraction peaks ascribed to isolated Zr and Y species are not observed in the patterns of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, it should be concluded that all the doped heteroatoms (Zr and Y) are highly dispersed in two types of samples, forming homogeneous solid solutions.

The areas were calculated according to the following equation, $A_{\text{Y}} = A(\text{Y } 3d_{5/2}) + A(\text{Y } 3d_{3/2})$, using a CasaXPS processing program.

3.1.3. Raman spectroscopy

Raman spectroscopy is one of the most effective methods to obtain a deep insight into the formation of oxygen vacancies in cerium-based catalysts [30,31,41–43]. To better understand the structural differences between $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, these materials were characterized using Raman spectroscopy,

which is more sensitive than XRD, to investigate and discuss the changes occurring in the solid solutions. As shown in Fig. 3(A) and (B), only one intense peak centered at 464 cm^{-1} , assigned to the F2g symmetry Raman vibration mode [44], was observed in CeO_2 , indicating its cubic fluorite-like structure. Moreover, the band at 464 cm^{-1} was well expressed in the Raman spectra of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$, $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$, $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, and $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$ when the heteroatoms (Zr and Y) were inserted into the lattice of CeO_2 , thus indicating that the cubic fluorite-like structure is still preserved in these catalysts. However, there were significant changes in the Raman peak intensities and widths, especially $\text{Ce}_{0.50}\text{Y}_{0.50}\text{O}_{2-\delta}$, which may be closely associated with the lattice distortion and/or the formation of oxygen vacancies in them; they might be attributed to the insertion of heteroatoms (Zr and Y) with different radii and valence states. As can be seen from Fig. 3 (inset), a broad and weak band located at 615 cm^{-1} was found in the spectra of both $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$; it may be assigned to structural defects arising from lattice distortion (expansion and/or contraction) owing to the disparity of ionic radius between Ce^{4+} and the doped cations (Zr^{4+} and Y^{3+}) [45,46]. Another weak band centered at around 560 cm^{-1} was clearly observed in the spectrum of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, but not in the spectrum of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$. The band was closely associated with the formation of oxygen vacancies [45,46], which originated due to the replacement of Ce^{4+} by Y^{3+} to maintain charge neutrality [47].

Based on the Raman results, it can be deduced that structural defects are generated within both $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$; however, the significant difference between $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ and $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ is that oxygen vacancies are formed only in Y-doped samples, but not in Zr-doped samples.

3.2. Relationship between surface lattice oxygen and catalytic activity

3.2.1. Catalytic activity

Fig. 3. (A) Raman spectra of CeO_2 (a), $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (b), $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (c), and $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ (d). (B) Raman spectra of CeO_2 (a), $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ (b), $\text{Ce}_{0.5}\text{Y}_{0.5}\text{O}_{2-\delta}$ (c), and $\text{Ce}_{0.25}\text{Y}_{0.75}\text{O}_{2-\delta}$ (d).

Fig. 4. Conversion of CH₃SH over Ce_{1-x}Zr_xO₂ (A) and Ce_{1-x}Y_xO_{2-δ} (B) samples ($x = 0, 0.25, 0.50$, and 0.75) at 350, 400, and 450 °C.

Fig. 4 shows the conversion of CH₃SH over Ce_{1-x}Y_xO_{2-δ}, Ce_{1-x}Zr_xO₂ ($x = 0.25, 0.50$, and 0.75), and CeO₂ at 350, 400, and 450 °C. According to Fig. 4, CH₃SH could be completely converted over the Ce_{1-x}Zr_xO₂ ($x = 0, 0.25$, and 0.50) and Ce_{1-x}Y_xO_{2-δ} ($x = 0$ and 0.25) catalysts when the reaction temperature was as high as 450 °C. Interestingly, the conversion of CH₃SH at 350, 400, and 450 °C initially increased with Zr loading ($x = 0.25$) and then decreased upon further addition ($x = 0.50$ and 0.75). However, within the reaction temperature range of 350 to 450 °C, the conversion of CH₃SH gradually decreased with increasing Y loading. Based on the above results, we can conclude that the addition of appropriate amounts of zirconium can improve the catalytic activity, while doped yttrium is not conducive to CH₃SH conversion.

To analyze the reason for the difference in the activities of Ce_{1-x}Zr_xO₂ and Ce_{1-x}Y_xO_{2-δ}, the best catalysts, Ce_{0.75}Zr_{0.25}O₂, Ce_{0.75}Y_{0.25}O_{2-δ}, and CeO₂ were chosen to explore the relation-

ship between the oxygen species and catalytic activity via a series of characterization techniques.

3.2.2. XPS

The O 1s and Ce 3d XPS spectra of Ce_{0.75}Zr_{0.25}O₂, Ce_{0.75}Y_{0.25}O_{2-δ}, and CeO₂ were recorded and presented in Fig. 5. Further, the corresponding data (surface lattice oxygen content, Ce³⁺ content, as well as the ratio of Ce³⁺ to Ce⁴⁺), calculated based on the XPS analysis of the three samples, are shown in Table 3. As displayed in Fig. 5(A), two photoelectron peaks were observed for CeO₂, Ce_{0.75}Zr_{0.25}O₂, and Ce_{0.75}Y_{0.25}O_{2-δ}, suggesting two types of oxygen species on their surfaces. The peak with the lower binding energy (529–530 eV) is the contribution of surface lattice oxygen (named as O_{S-latt}), while the other peak with higher binding energy, in the range of 531–533 eV, has been ascribed to surface adsorbed oxygen (denoted as O_{S-ads}) [8,48]. It could be seen by comparing Fig. 5(A) and Table 3 that

Fig. 5. O 1s (A) and Ce 3d (B) core level XPS spectra of CeO₂ (a), Ce_{0.75}Zr_{0.25}O₂ (b), and Ce_{0.75}Y_{0.25}O_{2-δ} (c).

Table 3O 1s and Ce 3d relative contents in CeO₂, Ce_{0.75}Zr_{0.25}O₂, and Ce_{0.75}Y_{0.25}O_{2-δ}.

Samples	Relative amount of O _{S-latt} ^a	Relative content of Ce	
		Ce ³⁺ /Ce ⁴⁺ ^c	Relative content of Ce ³⁺ ^b
CeO ₂	1.0000	0.2123	0.1751
Ce _{0.75} Zr _{0.25} O ₂	0.9995	0.2126	0.1753
Ce _{0.75} Y _{0.25} O _{2-δ}	0.9182	0.3688	0.2695

^aThe area of surface lattice oxygen of CeO₂ was assigned to be 1.0000, so as to compare with those of Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Y_{0.25}O_{2-δ}.^bThe relative content of Ce³⁺ was calculated according to Eqs. (1)–(3).^cThe Ce³⁺/Ce⁴⁺ ratio was calculated according to Eq. (4).

the O_{S-latt} relative content of Ce_{0.75}Zr_{0.25}O₂ was almost the same as that in CeO₂ and an analogous phenomenon was reported by Nelson and coworkers [49]. However, the O_{S-latt} relative content of Ce_{0.75}Y_{0.25}O₂ was significantly lower than those of CeO₂ and Ce_{0.75}Zr_{0.25}O₂. In comparison with CeO₂, the difference in the surface lattice oxygen contents of Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Y_{0.25}O₂ can be explained as follows. The incorporation of Zr⁴⁺ ions does not require charge compensation via the release of surface lattice oxygen (O_{S-latt}) to maintain charge neutrality as the chemical valence state of Zr⁴⁺ and Ce⁴⁺ is the same; on the other hand, when a Y³⁺ ion is inserted into the ceria lattice to replace Ce⁴⁺, in order to achieve charge neutrality, release of surface lattice oxygen (O_{S-latt}) to compensate for the charge difference between Y³⁺ ions and Ce⁴⁺ ions is indispensable. An analogous phenomenon was also observed for the substitution of Ce⁴⁺ ions with other low valence ions (M^{2+/3+}) [47].

The Ce 3d XPS spectra of CeO₂, Ce_{0.75}Zr_{0.25}O₂, and Ce_{0.75}Y_{0.25}O_{2-δ} are presented in Fig. 5(B). It is obvious that the Ce 3d XPS spectra of the three samples could be deconvoluted into 8 peaks, which were composed of pairs of spin orbit doublets. In general, the six peaks labeled as v, v', v'', u, u'', and u''' can be thought of as originating from the contributions of the Ce⁴⁺ state, whereas the peaks marked as v' and u' are ascribed to the contributions of Ce³⁺ [50]. According to previous studies

[24,51], the formulae listed below were employed to calculate the proportion of Ce³⁺ ions in the catalysts:

$$\text{Relative content of Ce}^{3+} = \{A_{v'} + A_{u'}\} / \{A_v + A_{v'} + A_{v''} + A_u + A_{u'} + A_{u''} + A_{v'} + A_{u'}\} \quad (1)$$

The ratio of Ce³⁺ and Ce⁴⁺ was calculated according to the following equation:

$$\text{Ce}^{3+}/\text{Ce}^{4+} = \{A_{v'} + A_{u'}\} / \{A_v + A_{v'} + A_{v''} + A_u + A_{u'} + A_{u''}\} \quad (2)$$

here, *A* is the Ce 3d photoelectron peak area and the results are shown in Table 3. It is noticeable that there is a significant decrease in all the Ce 3d photoelectron peak intensities of Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Y_{0.25}O_{2-δ} with respect to CeO₂, which may be due to the fact that the Ce ions have been substituted by Zr and Y ions. As can be seen from Table 3, the ratio of Ce³⁺ ions to Ce⁴⁺ ions and the relative content of Ce³⁺ in Ce_{0.75}Zr_{0.25}O₂ were comparable to those of CeO₂; however, the corresponding Ce³⁺/Ce⁴⁺ ratio and Ce³⁺ relative content in Ce_{0.75}Y_{0.25}O₂ were far higher than those of CeO₂. Generally, the switch change between Ce⁴⁺ and Ce³⁺ is usually accompanied the discharge of lattice oxygen [24]. The changes in the ratio of Ce³⁺/Ce⁴⁺ and the difference in the relative content of Ce³⁺ between Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Y_{0.25}O_{2-δ} should be related to the fact that some lattice oxygen can be removed from the latter, but not from the former. These results coincided with the results of O 1s characterization (Fig. 5(A) and Table 3).

From Fig. 4, we can determine that the conversion of CH₃SH over the three catalysts at reaction temperatures of 350 to 450 °C is in the order of Ce_{0.75}Zr_{0.25}O₂ > CeO₂ > Ce_{0.75}Y_{0.25}O_{2-δ}. Combined with the results of XPS, it can be deduced that the surface lattice oxygen (O_{S-latt}) may be associated with CH₃SH catalytic conversion.

To further investigate the action of O_{S-latt} in cerium oxides in CH₃SH decomposition, an example of CH₃SH transformation over CeO₂ was carried out at 450 °C for 10 h. Meanwhile, the corresponding O 1s XPS spectra at different reaction times are shown in Fig. 6. The O_{S-latt} relative contents in cerium dioxides at different reaction times are tabulated in Table 4. Obviously,

Fig. 6. (A) CH₃SH conversion during a time-on-stream test at 450 °C over CeO₂; (B) O 1s XPS spectra of CeO₂ before and after a time-on-stream test at 450 °C for various reaction times. (a) Fresh; (b) 1 h; (c) 3 h; (d) 6 h; (e) 10 h.

Table 4

Relative contents of surface lattice oxygen (O_{S-latt}) and Ce^{3+} in CeO_2 before and after a time-on-stream test for different time periods.

Samples	Relative content of O_{S-latt} ^a (%)	Relative content of Ce^{3+} ^b (%)
CeO_2 (0 h) ^c	100	16.0
CeO_2 (1 h) ^c	81.4	19.0
CeO_2 (3 h) ^c	49.8	29.5
CeO_2 (6 h) ^c	22.8	37.5
CeO_2 (10 h) ^c	19.8	41.9

^a The relative content of surface lattice oxygen (O_{S-latt}) was calculated from the O 1s spectra of CeO_2 before and after a time-on-stream test; the O_{S-latt} relative content of CeO_2 was set as 100%.

^b The relative content of Ce^{3+} was calculated according to Eqs. (1)–(3), using the Ce 3d spectra of CeO_2 before and after a time-on-stream test.

^c Reaction time of the time-on-stream test is included in the brackets.

CH_3SH conversion over CeO_2 decreased with the progress of the online reaction process, while the O_{S-latt} content in this catalyst declined. After 10 h, the conversion rate of methyl mercaptan over CeO_2 dropped to 88% and the O_{S-latt} content decreased to 20%. In contrast, during the reaction process, O_{S-ads} experienced a slight increase. The reason was that the O_{S-latt} content in CeO_2 could be consumed during the reaction, causing the formation of a greater amount of oxygen vacancies. These vacancies were able to catch some hydrate and carbonate species (CO and CO_2), which could be held responsible for the slight increase in the content of O_{S-ads} [52–54]. Therefore, the above results further show that O_{S-latt} directly influences CH_3SH conversion.

The relationship between O_{S-latt} and CH_3SH catalytic conversion was further analyzed from the Ce 3d XPS spectra of CeO_2 at different reaction times, as shown in Fig. 7. In addition, the corresponding computed results are also shown in Table 4. It

Fig. 7. Ce 3d XPS spectra of CeO_2 before and after a time-on-stream test at 450 °C for various time periods. (a) Fresh; (b) 1 h; (c) 3 h; (d) 6 h; (e) 10 h.

could be seen that photoelectron peak intensity ascribed to Ce^{4+} gradually declined with an increase in the online reaction time, while two other peaks attributed to the Ce^{3+} state increased with increasing time on the stream. The probable reason is that a large number of Ce^{4+} cations are transformed into Ce^{3+} cations after the online reaction period. According to literature, the shift between Ce^{4+} and Ce^{3+} is usually accompanied by oxygen release in the cerium lattice [24] and thus, O_{S-latt} can take part in the methanethiol conversion process.

According to these results acquired from active experiments as well as other characterization techniques, two conclusions can be made. Firstly, O_{S-latt} , rather than O_{S-ads} , plays an important role in CH_3SH conversion over ceria-based materials. Second, the difference in activity between the two heteroatoms (Zr and Y)-doped cerium based catalysts ($Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Y_{0.25}O_{2-\delta}$) is because of the incorporation of Y^{3+} into the CeO_2 lattice causing the removal of O_{S-latt} for maintaining electric neutrality. The insertion of Zr^{4+} ions need not release surface lattice oxygen (O_{S-latt}) to maintain charge neutrality due to the same chemical valence states of Zr^{4+} and Ce^{4+} . Thus, $Ce_{0.75}Zr_{0.25}O_2$ exhibits better catalytic activity.

3.2.3. H_2 -TPR

The H_2 -TPR patterns of CeO_2 , $Ce_{0.75}Zr_{0.25}O_2$, and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ are presented in Fig. 8 to investigate their redox properties. It could be found that CeO_2 exhibited two obvious reduction peaks in range of 400–800 °C, ascribed to the reduction of surface oxygen and bulk oxygen species separately [55]. Compared with CeO_2 , both $Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ exhibited just a single reduction peak in the region between 400 and 650 °C. This is because when the temperature is increased from 100 to 900 °C, surface and bulk reduction occur concurrently; in other words, there is no clear distinction between the

Fig. 8. H_2 -TPR profiles of CeO_2 (a), $Ce_{0.75}Zr_{0.25}O_2$ (b), and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ (c).

surface and bulk peaks, which suggests that the oxygen species located within the subsurface or bulk of these two samples can migrate to the surface of the catalysts as surface oxygen to be consumed [56,57]. Moreover, it was noted that the H_2 consumption of $Ce_{0.75}Zr_{0.25}O_2$ at low temperatures (around 500 °C) was larger than those of CeO_2 and $Ce_{0.75}Y_{0.25}O_{2-\delta}$, thus showing that more oxygen species have been reduced.

Based on the characterization results of XPS and H_2 -TPR, the difference in the catalytic activities of CeO_2 , $Ce_{0.75}Zr_{0.25}O_2$, and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ can be explained as follows. When $Ce_{0.75}Zr_{0.25}O_2$ is compared with CeO_2 , the O_{S-latt} amounts of CeO_2 and $Ce_{0.75}Zr_{0.25}O_2$ are almost the same, whereas the redox properties of the latter are better than those of the former. Therefore, the catalytic activity of $Ce_{0.75}Zr_{0.25}O_2$ is higher than that of CeO_2 . As for $Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Y_{0.25}O_{2-\delta}$, their redox properties are almost the same, while the O_{S-latt} amount in $Ce_{0.75}Zr_{0.25}O_2$ is higher than that in $Ce_{0.75}Y_{0.25}O_{2-\delta}$. Accordingly, the catalytic activity of $Ce_{0.75}Zr_{0.25}O_2$ is higher than that of $Ce_{0.75}Y_{0.25}O_{2-\delta}$. The difference in the activities of $Ce_{0.75}Y_{0.25}O_{2-\delta}$ and CeO_2 is related to the fact that the O_{S-latt} amount of the former is lower than that of the latter.

3.3. The relationship between bulk lattice oxygen migration and catalytic stability

3.3.1. Catalytic stability

The catalytic conversions of CH_3SH with reaction time below 450 °C over CeO_2 , $Ce_{0.75}Zr_{0.25}O_2$, and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ are shown in Fig. 9. Interestingly, the catalytic stability of $Ce_{0.75}Y_{0.25}O_{2-\delta}$ obviously improved, when compared to those of $Ce_{0.75}Zr_{0.25}O_2$ and CeO_2 , while there was not much change in the catalytic stability over CeO_2 and $Ce_{0.75}Zr_{0.25}O_2$ (Fig. 9). Therefore, the difference in the catalytic life of CeO_2 , $Ce_{0.75}Zr_{0.25}O_2$, and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ will be investigated and discussed in the fol-

lowing sections.

According to the H_2 -TPR characterization results (Fig. 8), only one reduction peak was observed for both $Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ in the region of 400–650 °C, which indirectly verified the mobility of the subsurface or bulk lattice oxygen to the surface of catalysts as surface oxygen to be consumed [51,52,56,57]. Furthermore, the Raman characterization results showed that oxygen vacancies were formed only in $Ce_{0.75}Y_{0.25}O_{2-\delta}$ but not in $Ce_{0.75}Zr_{0.25}O_2$ (Fig. 3). It has been well documented that the formation of oxygen vacancies is in favor of the mobility of bulk lattice oxygen (O_{B-latt}) [58]. In our previous work, it was proven that the rapid deactivation of CeO_2 is closely related to the depletion of O_{S-latt} . Thus, we postulated that the improved catalytic life of $Ce_{0.75}Y_{0.25}O_{2-\delta}$, as compared to those of $Ce_{0.75}Zr_{0.25}O_2$ and CeO_2 , may be due to the migration of O_{B-latt} to rapidly replenish O_{S-latt} . Moreover, the difference in the catalytic stabilities of $Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ may be related to the fact that the O_{B-latt} migration rate of $Ce_{0.75}Zr_{0.25}O_2$ is slower than that of $Ce_{0.75}Y_{0.25}O_{2-\delta}$ owing to the absence of oxygen vacancies.

3.3.2. Analysis of oxide products

In order to verify our postulation that the rapid migration of O_{B-latt} is responsible for the improvement in catalytic stability and reconfirm the role of O_{S-latt} in improving the catalytic activity, the concentration of reaction products including CO and CO_2 during the CH_3SH catalytic conversion process over $Ce_{0.75}Zr_{0.25}O_2$ and $Ce_{0.75}Y_{0.25}O_{2-\delta}$ were investigated. The corresponding results are shown in Fig. 10. At the beginning (3 h), the product concentrations of CO and CO_2 over $Ce_{0.75}Zr_{0.25}O_2$ were higher than those on $Ce_{0.75}Y_{0.25}O_{2-\delta}$, which provided direct proof that more surface oxygen species in $Ce_{0.75}Zr_{0.25}O_2$ participated in the decomposition of CH_3SH . This is because the amount of O_{S-latt} in $Ce_{0.75}Zr_{0.25}O_2$ is higher than that in

Fig. 9. CH_3SH conversion as a function of reaction time at 450 °C on CeO_2 , $Ce_{0.75}Zr_{0.25}O_2$, and $Ce_{0.75}Y_{0.25}O_{2-\delta}$.

Fig. 10. CO (a) and CO_2 (b) concentrations on $Ce_{0.75}Zr_{0.25}O_2$ and CO (c) and CO_2 (d) concentrations on $Ce_{0.75}Y_{0.25}O_{2-\delta}$ as functions of reaction time.

$\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, as shown in Fig. 5(A) and Table 3. Furthermore, with an increase in the reaction time up to 5 h, the CO concentration of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ could be compared with that of $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, while a small amount of CO_2 was observed in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ but not in $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$. This may be because of the presence of an adequate concentration of surface lattice oxygen leading to the oxidation of CO. However, the concentration of $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ was universally higher than that of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ after 8 h. What's more, an ideal situation was observed; $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ contained more than 750 ppm of CO after 12 h of an online reaction test, whereas the corresponding CO concentration in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ approached zero under the same conditions. This phenomenon can be conceivably illustrated as shown below. $\text{O}_{\text{S-latt}}$ is gradually consumed during the online reaction period; on the other hand, $\text{O}_{\text{B-latt}}$ in $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ quickly migrates to the surface of the catalyst to supplement the consumed $\text{O}_{\text{S-latt}}$.

3.3.3. OSC analysis

OSC measurements were also performed in a successive CO pulse mode to study the effect of oxygen storage capacity on bulk lattice oxygen migration (Fig. 11). The quantitative data of OSC and TOSC over $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ samples are summarized in Table 5. For the first CO pulse over $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, compared with $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$, it could be seen that there was a greater amount of CO consumption and CO_2 production. In addition, the OSC and TOSC of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ were higher than those of $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ (Table 5), manifesting that plenty of the most active and accessible oxygen species exist in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ than in $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$. Those available oxygen species contribute to the oxidation of CO, corresponding to the results of product analysis shown in Fig. 10, indicating the formation of more CO_2 over $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ during the first several hours. However, after the third pulse, as shown in Fig. 11, $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ could consume more carbon monoxide (Fig. 11(A)) and produce more carbon dioxide (Fig. 11(B)) as com-

Table 5

OSC and TOSC analysis of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$.

Sample	OSC ^a ($\mu\text{mol [O]}/\text{g}$)	TOSC ^a ($\mu\text{mol [O]}/\text{g}$)
$\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ ^b	602	1831
$\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ ^b	297	1571

^a Oxygen contents according to CO pulses

^b CO pulses with 100% CO at 450 °C for 1 h.

pared to $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, which indicates that the former possesses greater oxygen mobility. The above results also offer direct evidence that the mobility rate of $\text{O}_{\text{B-latt}}$ in $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ is superior to that in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$.

3.4. Influence of valence and ionic radius on catalytic activity and stability

Combining the above described experimental results with the relevant characterization results, the influence of the doped heteroatom's valence and ionic radius on the catalytic activity and stability for CH_3SH decomposition over ceria-based catalysts will be discussed. Fig. 12 shows a schematic diagram of heteroatom (M) modified ceria-based solid solutions.

In heteroatom (M) doped ceria-based materials, doping low valence M ($\text{M}^{2+/3+}$) ions will cause a loss of lattice oxygen, generating more quantitative oxygen vacancies, promoting the migration of bulk lattice oxygen in the catalysts so as to improve their catalytic stability; however, it is not conducive to enhancing their activity due to the removal of surface lattice oxygen. In comparison, M^{4+} -doped cations do not lead to the loss of lattice oxygen, which is beneficial in improving the activity of ceria-based catalysts. However, they go against bulk lattice oxygen migration because of the lack of oxygen vacancies, owing to which the stability of the material deteriorates. The difference in radius between Ce and M ions leads to defect species, which couldn't work for increasing bulk lattice oxygen mobility as to improve the stability of ceria-based catalysts.

Fig. 11. The pulse signals of CO (A) and CO_2 (B) during a CO multi-pulse test over $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ at 450 °C.

Fig. 12. Schematic diagram of heteroatom modified ceria-based solid solutions.

4. Conclusions

In this work, a series of $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0.25, 0.50, 0.75$, and 1.0), and CeO_2 catalysts were rapidly prepared by a citric acid complexation method using microwaves. The catalytic behavior of these materials for the decomposition of CH_3SH was analyzed, along with a series of other characterization techniques, to investigate the role of oxygen vacancies and the relationship between the oxygen species and catalytic properties. The results showed that surface lattice oxygen plays a key role in CH_3SH catalytic conversion. $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ shows higher catalytic activity for the decomposition of CH_3SH due to more surface lattice oxygen and readily available oxygen species, along with better redox properties. $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ exhibits better catalytic stability compared to CeO_2 and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. This is because more oxygen vacancies within $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ can promote bulk lattice oxygen migration in order to replenish surface lattice oxygen and improve its catalytic stability. The valence difference between Ce and the heteroatom seriously affects the quantity of surface lattice oxygen and mobility of bulk lattice oxygen within ceria-based catalysts, thus influencing catalytic activity and stability for CH_3SH conversion. Moreover, the difference in the radii of Ce and the heteroatom will lead to the formation of defect species that cannot promote bulk lattice oxygen mobility or improve the catalytic stability of cerium-based catalysts.

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Relationship between oxygen species and activity/stability in heteroatom (Zr, Y)-doped cerium-based catalysts for catalytic decomposition of CH_3SH

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Surface lattice oxygen plays a key role in decomposing CH_3SH . Oxygen vacancies promote bulk lattice oxygen migration. The valence difference between the doped ions affects the catalytic behavior.

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杂原子(Zr, Y)掺杂的铈基催化剂中氧物种与其催化 CH_3SH 分解的活性/稳定性之间的关系

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摘要: 铈基催化剂因其优异的储放氧能力被广泛地应用于多种催化反应. 铈基材料作为催化剂在 CH_3SH (甲硫醇) 分解反应中的应用也因产物简单、易处理而受到越来越多的关注. 本课题组在前期研究中发现, 纳米二氧化铈在 CH_3SH 催化分解反应中表现出较高的催化活性, 然而催化剂却在很短时间内快速失活. 为进一步提高铈基氧化物的稳定性, 我们通过引入稀土元素对氧化铈催化剂进行改性, 结果发现其稳定性明显提高; 同时催化剂稳定性与氧空位数量有关, 氧空位数量

越多, 催化剂越稳定. 然而, 目前关于氧空位对催化 CH_3SH 分解反应的具体作用, CH_3SH 在铈基材料上的失活机理以及氧物种与催化行为之间的相互关系尚不清楚. 因此, 有必要进一步研究氧空位对提高催化稳定性的贡献并揭示催化行为与氧物种之间的相互关系.

本文通过微波辅助柠檬酸络合法制备一系列杂原子(Zr, Y)掺杂的铈基催化剂 CeO_2 , $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$, $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ ($x = 0.25, 0.50, 0.75, 1.00$), 通过考察铈、钇杂原子价态和离子半径对 CH_3SH 催化分解活性和稳定性的影响来探索铈基催化剂中氧空位的作用及氧物种与催化行为之间的关系. 其中, 氧物种与催化行为之间的关系可包括两类: (1) 表面晶格氧与催化活性之间的关系; (2) 体相晶格氧迁移与催化稳定性之间的关系.

催化性能和表征结果表明, 铈基氧化物中表面晶格氧对 CH_3SH 催化转化起着至关重要的作用. $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ 在 CH_3SH 的催化分解中表现出更高的催化活性, 这是由于 $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ 有更多的表面晶格氧、活性氧物种及良好的氧化还原性能. $\text{Ce}_{0.75}\text{Y}_{0.25}\text{O}_{2-\delta}$ 也表现出更好的催化稳定性, 这是由于催化剂中有更多的氧空位, 它们会促进体相晶格氧迁移到催化剂表面以补充表面晶格氧. 此外, Ce与杂原子之间化学价差极大地影响着表面晶格氧含量以及催化剂中体相氧的迁移率, 进而影响铈基催化剂的活性和稳定性.

关键词: 铈基催化剂; 杂原子; 表面晶格氧; 甲硫醇分解; 体相氧迁移

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