

Article Synthesis and Oxygen Storage Capacities of Yttrium-Doped CeO₂ with a Cubic Fluorite Structure

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Abstract: Doping CeO₂ with Y cations was achieved in this study using three strategies: doping only during the hydrothermal process (H-Y-doped CeO₂), doping only during the impregnation process (I-Y-doped CeO₂), and doping during both the hydrothermal and impregnation processes (H/I-Y-doped CeO₂). During the three synthesis strategies of Y-doped CeO₂, these Y ions could be incorporated into the CeO₂ lattice in the +3 state while holding the cubic fluorite structure, and no impurity phases were detected. Pure CeO₂ crystal itself contained a certain number of intrinsic *V*_O defects, and Y-doping was beneficial for the creation of extrinsic *V*_O defects. The relative concentrations of *V*_O defects were quantified by the values of *A*₅₉₂/*A*₄₆₄ obtained from Raman spectra, which were 1.47, 0.93, and 1.16 for the H-Y-, I-Y-, and H/I-Y-doped CeO₂, respectively, and were higher than that of the undoped one (0.67). Moreover, the OSCs of the three Y-doped CeO₂ (0.353 mmol/g) > I-Y-doped CeO₂ (0.248 mmol/g) > Undoped CeO₂ (0.153 mmol/g); this result was in good agreement with the Raman spectroscopy results.

Keywords: CeO₂; rare-earth; doping; hydrothermal; impregnation; oxygen storage capability

1. Introduction

With the continuous development of science and technology, the development and utilization of energy and resources have become a hot topic [1–3]. Rare-earth elements, known as "industrial monosodium glutamate", "industrial vitamin", and "mother of new materials", are precious strategic metal resources. Cerium (Ce) is the most abundant rare-earth element in the Earth's crust. Its common valence states are +3 and +4, and the corresponding oxides are cerium sesquioxide (Ce_2O_3) and cerium dioxide (CeO_2) [4–6]. Ce₂O₃ is unstable in air and easily oxidizes to CeO₂. Interestingly, there are not only Ce⁴⁺ ions in CeO₂ crystals but also trace amounts of Ce³⁺ ions. The oxidation/reduction cycle composed of Ce^{3+} and Ce^{4+} states ($Ce^{3+}\leftrightarrow Ce^{4+}$) enables CeO_2 to store and release oxygen, referred to as oxygen storage capability (OSC). In other words, CeO₂ can release oxygen under reducing conditions, forming nonstoichiometric oxides CeO_{2-x} , and the CeO_{2-x} can store oxygen by filling oxygen vacancies under oxidizing conditions [7,8]. In the atmosphere or an oxygen-rich environment, CeO_2 can store some oxygen in its own lattice, and these stored oxygen atoms can be released quickly when the partial pressure of ambient oxygen decreases. Precisely because of this ability, CeO₂ is considered an excellent catalyst in CO_2 methanation [9,10], hydrodeoxygenation of xylitol and fatty acids [11,12], NO_x conversion [13,14], and so on.



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Doping the CeO_2 lattice with other metallic elements has been proven to be an effective method to improve the OSC of CeO₂. These include rare-earth elements (Sm [15], La, Pr, Nd, and Pm [16]), transition-metal elements (Fe [17], Ni [18], Co [19], Mn, and Cu [20]), earth-alkaline elements (Be, Mg, Ba, and Sr [21]), and noble-metal elements [22]. Among many impurity elements, the incorporation of rare-earth elements into the CeO₂ lattice should be relatively easy because the impurity rare-earth metallic ions and Ce ions have a similar ionic size and electronic structure. To date, numerous methods have been used to synthesize rare-earth-doped CeO₂, including the co-precipitation method [23], metalorganic chemical vapor deposition (MOCVD) [24], the solid-state reaction (SSR) method [25], the sol–gel method [26], and flame spray pyrolysis [27]. Among the many methods for doping CeO₂, the hydrothermal method is considered to be one of the most effective. A Teflonlined stainless-steel autoclave is employed in the hydrothermal synthesis process, and the closed reaction environment can breed a high-pressure environment under the action of heating, which is conducive to integrating impurity ions into the lattice of CeO_2 or cerium precursor [28,29]. In addition, the impregnation method also has attracted an increasing amount of attention recently because the operation of this technique is simple and efficient, especially for doping onto the CeO_2 surface [30,31].

In this work, the Y element was introduced into the CeO₂ lattice by three routes in the same system, using the same cerium source (Ce(NO₃)₃·6H₂O) and dopant (Y(NO₃)₃·6H₂O). The first route involved the incorporation of Y ions during only the hydrothermal process, whereas the second route involved the incorporation of Y ions during only the impregnation process, and the third route involved the incorporation of Y ions during both the hydrothermal and impregnation processes. The characterizations of the phase composition, lattice parameters, quantitative concentration of Ce³⁺, and oxygen vacancy of these as-synthesized Y-doped CeO₂ were investigated and discussed in detail. Moreover, a comparative analysis was also performed. Subsequently, the OSC of CeO₂ was examined and quantified using O₂ temperature-programmed desorption (O₂-TPD) measurements.

2. Experimental Section

2.1. Starting Materials

 $Ce(NO_3)_3 \cdot 6H_2O$ (99.95%) and $Y(NO_3)_3 \cdot 6H_2O$ (99.99%) were supplied by Aladdin Co., Ltd. (Shanghai, China) and Maclin Biochemical Technology Co., Ltd. (Shanghai, China), respectively. Ethylene glycol (EG, 99.5%) and acid orange 7 (AO7, 97.0%) were supplied by Chengdu Kelong Chemical Co., Ltd. (Chengdu, China) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), respectively. Distilled water was used in all experiments. All major chemicals were used as received without further purification.

2.2. Synthesis of Y-Doped CeO₂ Powders

A flow chart of the synthesis procedures employed for the undoped and Y-doped CeO₂ samples is shown in Figure 1. The reference CeO₂ without Pr-doping was prepared by the hydrothermal process using Route 1 (R1), as shown in Figure 1, denoted as Undoped CeO₂. The CeO₂ samples doped with Pr cations during only the impregnation process or the hydrothermal process were synthesized as shown in Route 2 (R2) and Route 3 (R3) of Figure 1, denoted as I-Y-doped CeO₂ and H-Y-doped CeO₂, respectively, while the one doped during both the impregnation and hydrothermal processes was synthesized as shown in Route 4 (R4) of Figure 1, denoted as H/I-Y-doped CeO₂.

Undoped CeO₂ was synthesized using R1: 4.0 mmol Ce(NO₃)₃·6H₂O, 25 mL EG, and 5 mL distilled water were added into a 50 mL Teflon-lined stainless-steel autoclave and sealed at 200 °C for 24 h. Afterward, the Ce precursor was collected, washed, and dried in turn. Finally, Undoped CeO₂ was obtained by subsequent calcination in air at 500 °C for 2 h.

I-Y-doped CeO₂ was synthesized using R2: the Ce precursor synthesized in R1 was impregnated into a saturated solution of Y^{3+} ions at room temperature for 24 h. After

filtration and drying, the I-Y-doped CeO₂ was obtained by subsequent calcination in air at 500 $^{\circ}$ C for 2 h.

H-Y-doped CeO₂ was synthesized using R3: 3.84 mmol Ce(NO₃)₃·6H₂O, 0.16 mmol Y(NO₃)₃·6H₂O, 25 mL EG, and 5 mL distilled water were added into a 50 mL Teflon-lined stainless-steel autoclave and sealed at 200 °C for 24 h. Afterward, the Ce/Y precursor was collected, washed, and dried in turn. Finally, H-Y CeO₂ was obtained by subsequent calcination in air at 500 °C for 2 h.

H/I-Y-doped CeO₂ was synthesized using R4: the Ce/Y precursor synthesized in R3 was impregnated into a saturated solution of Y^{3+} ions at room temperature for 24 h. After filtration and drying, the H/I-Y-doped CeO₂ was obtained by subsequent calcination in air at 500 °C for 2 h.



Figure 1. Schematic illustration of the synthesis of undoped and Y-doped CeO₂ using three routes.

2.3. Characterization

The crystallographic phases of the samples were characterized by X-ray diffraction (XRD, DX-2700). The surface composition and binding energy of the CeO₂ samples were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, Waltham, MA, USA). The oxygen vacancy (V_O) defects of the CeO₂ samples were characterized using a Raman spectrometer (LabRAM Aramis, Horiba Jobin-Yvon, Paris, France) with a He–Cd laser of 325 nm, and the exposure time for the measurement set was 60 s.

2.4. OSC

The OSC of CeO₂ was estimated using O₂ temperature-programmed desorption (O₂-TPD) measurements, which were carried out in a plug-flow microreactor system (TP5000) with a thermal conductivity detector, and the amount of O₂ desorption during the process was measured by the thermal conductivity detector. About 0.1 g of CeO₂ powder was activated using an air stream at 400 °C for 30 min, then moved into He and cooled,

then exposed to an air stream for 30 min at 120 °C, followed by purging with a He stream to remove the excess O₂. Finally, the surface oxygen desorption was conducted at a flow rate of He (10 mL/min) while the temperature was raised to ~900 °C (10 °C/min).

3. Results and Discussion

XRD was employed to characterize the phase composition of the as-synthesized undoped and Y-doped samples. Figure 2 shows the XRD patterns of the Undoped CeO₂ and H-Y-, I-Y-, and H/I-Y-doped CeO₂ powders. For the XRD pattern of the Undoped CeO₂, eight well-resolved peaks were observed, which could be indexed to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of cubic CeO₂ (JCPDS no. 34-0394; fluorite). No additional phases were detected, suggesting pure CeO_2 had been obtained by the hydrothermal process using route R1 in Figure 1. After the introduction of Y cations in the synthesis process, the XRD patterns of the H-Y-, I-Y-, and H/I-Y-doped CeO_2 samples exhibited a similar profile to that of the Undoped CeO_2 . However, no peaks for impurity phases such as Y_2O_3 were detected, which could be explained as follows: the impurities in Y-doped CeO_2 samples might exist as highly dispersed or amorphous surface species, or the amount of the Y impurity was low. Another possibility is that the Y cations partially substituted the Ce ions to form a solid solution. The inset in Figure 2 shows that the (111) reflection shifts toward lower 2θ values with the incorporation of Y ions, and it can be found that the shift exhibited by the H-Y-doped CeO₂ sample was the greatest. Moreover, the lattice parameters of CeO₂ were estimated using Bragg's equation and summarized in Table 1. It was found that the calculated lattice parameters for H-Y- (5.4242 Å), I-Y-(5.4190 Å), and H/I-Y-doped (5.4227 Å) CeO₂ were greater than that of the undoped sample (5.4117 Å). These findings implied that the large Y ions (1.02 Å) partially substituted the Ce^{4+} ions (0.97 A [32]) to form a CeO₂-based solid solution while holding the cubic fluorite structure of CeO_2 .

Table 1. Phase, lattice parameters, $[Ce^{3+}]_{XPS}$, $[V_O]_{XPS}$, $[V_O]_{Raman}$, and [OSC] of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂.

Parameter Sample Name	Undoped	H-Y Doped	I-Y Doped	H/I-Y Doped
Phase from XRD	CeO ₂	CeO ₂	CeO ₂	CeO ₂
Lattice parameters (Å)	5.4117	5.4242	5.4190	5.4227
$[Ce^{3+}]_{XPS}$ (%)	6.54	12.60	8.95	11.37
[V _O] _{XPS} (%)	24.36	30.65	26.32	28.72
$[V_{\rm O}]_{\rm Raman}$	0.67	1.47	0.93	1.16
$[OSC] (mmol O_2/g CeO_2)$	0.153	0.372	0.248	0.353

In order to probe the possibility of the presence of the Y element in CeO₂, as well as the chemical state of its presence, XPS was employed to study the Undoped CeO₂ and Y-doped CeO₂. Figure 3a shows the wide-scan XPS spectra of the Undoped CeO₂ and H-Y-, I-Y-, and H/I-Y-doped CeO₂ powders. As observed in Figure 3a, the XPS profiles of all the samples were similar, dominated by the signals of Ce, O, and C elements, in accordance with a previous report for pure and Y-doped CeO₂ [33]. However, there was no sign of the Y element at first sight from the wide-scan XPS spectra of the H-Y-, I-Y-, and H/I-Y-doped CeO₂. To ascertain whether the CeO₂ contained the Y cations and the Y-doping was real, the corresponding Y 3d XPS regions of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ were recorded. For the Y 3d XPS regions of the H-Y- and H/I-Y-doped CeO₂, we could cleanly identify the Y 3d signal and its unique contour, which is assigned to the trivalent Y ions. However, the Y signal was weak from the Y 3d XPS regions of the I-Y-doped CeO₂, yet its signal peak of Y 3d could still be identified in graphing alone (inset in Figure 3b).



Figure 2. XRD patterns of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂ powders (the inset shows the (111) reflection shifts using a smaller scan speed of 0.01° /min).



Figure 3. (a) Wide-scan XPS spectra of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂ and (b) the corresponding XPS regions of Y 3d for H-Y-, I-Y-, and H/I-Y-doped CeO₂ (the inset in Figure 3b is an independent drawing of the Y 3d XPS region for I-Y-doped CeO₂).

In order to understand the effect of Y-doping on Ce ions in CeO₂ crystals, the Ce 3d XPS regions of the Undoped CeO₂ and H-Y-, I-Y-, and H/I-Y-doped CeO₂ were recorded and fitted, as shown in Figure 4. The Ce 3d core-level XPS of all CeO₂ samples could be fitted into eight peaks, referring to the $3d_{5/2}$ and $3d_{3/2}$ spin-orbit doublet of Ce cations (including Ce³⁺ and Ce⁴⁺ ions). The bonds labeled as v_2 and u_2 belong to the spin-doublet term of the Ce³⁺ state, and the bands labeled as v_4 , v_3 , and v_1 (and those for u) are due to the case of the Ce⁴⁺ state [34]. A quantitative analysis of the concentration of Ce³⁺ ions based on the measured Ce 3d XPS spectra, labeled as $[Ce^{3+}]_{XPS}$, could be performed using Equation (1), and the results are summarized in Table 1. The $[Ce^{3+}]_{XPS}$ values of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ (6.54%), indicating that pure CeO₂ crystal itself contains a certain number of Ce³⁺ ions and that Y-doping could promote the formation of Ce³⁺ species, especially H-Y-doped CeO₂, which exhibited the highest $[Ce^{3+}]_{XPS}$ values. The Ce³⁺ species in pure CeO₂ contributed to the OSC of CeO₂ through the oxidation/reduction cycle composed of Ce³⁺ and Ce⁴⁺ states (Ce³⁺ $\leftrightarrow Ce^{4+}$).

$$[Ce^{3+}]_{XPS}(\%) = \frac{A_{u_2} + A_{v_2}}{A_{u_4} + A_{u_3} + A_{u_2} + A_{u_1} + A_{v_4} + A_{v_3} + A_{v_2} + A_{v_1}} \times 100$$
(1)

where A_i is the integrated area of the *i*th fitting peak from Ce 3d XPS spectra.



Figure 4. Ce 3d XPS spectra of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂.

In order to understand the effect of Y-doping on oxygen ions in CeO₂ crystals, the O 1s XPS regions of the Undoped CeO₂ and H-Y-, I-Y-, and H/I-Y-doped CeO₂ were recorded and fitted, as shown in Figure 5. The O 1s XPS spectrum of the Undoped CeO₂ was curve-fitted into two peaks: one peak, labeled as α , at ~529.2 eV, could be attributable to the lattice oxygen species; the other peak, labeled as β , at ~531.4 eV, could be attributable to the chemisorbed oxygen species and/or weakly bonded oxygen species related to the oxygen vacancy (V_{O}) defects. For the O 1s spectra of the H-Y-, I-Y-, and H/I-Y-doped CeO₂, a new peak labeled as γ , at~528.5 eV, was curve-fitted, which could be assigned to the O-Y species. In addition, the relative oxygen vacancies ratio (labeled as [V_{O}]_{XPS}) could be quantified using Equation (2), and the results are shown in Table 1.

$$[V_{\rm O}]_{\rm XPS}(\%) = \frac{A_{\beta}}{A_{\alpha} + A_{\gamma} + A_{\beta}} \times 100 \tag{2}$$

where A_i is the integrated area of the *i*th fitting peak from O 1s XPS spectra. As observed in Table 1, the $[V_O]_{XPS}$ values of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ were 30.65%, 26.32%, and 28.72%, respectively, which are higher than that of the undoped sample (24.36%). The results indicate that pure CeO₂ crystal itself contained a certain number of V_O species (namely intrinsic V_O defects) and that Y-doping was beneficial for the creation of V_O defects, especially H-Y-doped CeO₂, which exhibited the highest $[V_O]_{XPS}$ values.

To further investigate the $V_{\rm O}$ defects, Raman spectra of CeO₂ were obtained. Raman spectroscopy is a powerful tool for the structural characterization of metal oxides due to its sensitivity to structural changes, such as $V_{\rm O}$ defects. Figure 6 shows the Raman spectra of the Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂. For the Undoped CeO₂, the spectral envelope in the 200~1000 cm⁻¹ range displayed a strong band at 464 cm⁻¹ associated with the triply degenerate F_{2g} vibrational mode of CeO₂ [35,36], while the band located at 592 cm⁻¹ was associated with the optical LO mode of substoichiometric CeO_{2-x} units, underscoring an increase in $V_{\rm O}$ defects [37,38]. Upon Y-doping, increases in the intensity of the bands located at 464 and 592 cm⁻¹ were observed for the H-Y-, I-Y-, and H/I-Y-doped CeO₂, which were associated with the presence of substoichiometric CeO_{2-x}, underscoring an increase in $V_{\rm O}$ defects. However, the Y³⁺-doping into the CeO₂ lattice

increased its lattice distortion and hence interfered with the vibrations of CeO₂. Therefore, the Raman band intensities of the Y-doped CeO₂ were clearly affected by the incorporation of Y^{3+} into the CeO₂ lattice. Consequently, an alternative approach to estimate the relative concentration of V_O defects can be adopted by calculating the ratio of the integrated area of the Raman band at 592 cm⁻¹ to that of 464 cm⁻¹ (labeled [V_O]_{Raman}) [39,40]. The values of A_{592}/A_{464} , that is, the relative concentration of oxygen vacancies ([V_O]_{Raman}), are shown in Table 1. It can be seen that the [V_O]_{Raman} values of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ were 1.47, 0.93, and 1.16, respectively, which are higher than that of the undoped sample (0.67).



Figure 5. O 1s core-level XPS spectra of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO2.



Figure 6. Raman spectra of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂.

According to the Ce 3d XPS analyses in Figure 4, it can be seen that pure CeO₂ had a certain number of Ce³⁺ ions, contributing to the OSC of CeO₂ with the formation and filling of intrinsic $V_{\rm O}$ defects, which could be expressed by Equation (3) and written using Kroger

and Vink notations as in Equation (4). In the synthesis of CeO₂, Y ions were introduced and doped into the CeO₂ lattice, and a substoichiometric CeO_{2-x} unit was formed with an increase in V_O defects. The creation of extrinsic V_O defects could be expressed by Equations (5) and (6). The vacancy compensation mechanism has been suggested for the increased concentration of V_O for Y-doping into CeO₂. As shown in Equations (3) and (4), besides the intrinsic V_O in CeO₂, there are two additional kinds of V_O : one V_O is created to balance the charge when two adjacent Ce⁴⁺ cations are substituted by two Y³⁺ cations, as shown in Equation (5); and substitution of one Ce⁴⁺ by one Y³⁺ gives rise to the formation of one V_O with the adjacent Ce⁴⁺ reduced to Ce³⁺, as shown in Equation (6).

$$\operatorname{CeO}_{2} \xleftarrow{\operatorname{Oxygen release}}_{\operatorname{Oxygen storage}} \operatorname{Ce}_{1-x}^{4+} \operatorname{Ce}_{x}^{3+} \operatorname{O}_{2-x/2}(V_{O})_{x/2} + x/4\operatorname{O}_{2}$$
(3)

$$Ce_2O_3 \xrightarrow{2CeO_2} 2Ce'_{Ce} + 3O_O^{\times} + V_O^{\bullet\bullet}$$
(4)

$$Y_2O_3 \xrightarrow{2CeO_2} 2Y'_{Ce} + 3O_O^{\times} + V_O^{\bullet\bullet}$$
(5)

$$Y_2O_3 + Ce_2O_3 \xleftarrow{2CeO_2} Y'_{Ce} + Ce'_{Ce} + 3O_O^{\times} + V_O^{\bullet\bullet}$$
(6)

where Y'_{Ce} represents a Y^{3+} cation occupying the site of a Ce⁴⁺ cation and Ce'_{Ce} represents a Ce³⁺ cation occupying the site of a Ce⁴⁺ cation. V_O and $V_O^{\bullet\bullet}$ represent an oxygen vacancy defect and one with two positive charges, respectively, which are produced via the vacancy compensation mechanism; and O_O^{\bullet} is a lattice oxygen atom. From the O 1s XPS analysis in Figure 5 and the Raman analysis in Figure 6, it can be seen that pure CeO₂ crystal itself contained a certain number of V_O species (namely intrinsic V_O defects), which exhibited a large deviation from stoichiometry in the atmosphere, forming nonstoichiometric oxide CeO_{2-x}. After doping with Y³⁺ cations, CeO₂ could still retain its fluorite crystal structure (see Figure 2), accompanied by the loss of oxygen from its lattice and the consequent formation of a large number of extrinsic V_O defects (see Table 1, Figures 5 and 6).

Table 2 shows the lattice parameters, $[Ce^{3+}]_{XPS}$, $[V_O]_{XPS}$, and $[V_O]_{Raman}$ of undoped and Y-doped CeO₂ from recent literature [41–43]. By comparing these data of undoped and Y-doped CeO₂, we could find that the lattice expansion occurred upon the incorporation of Y³⁺ into the CeO₂ lattice, accompanied by the presence of Ce³⁺ ions and more V_O defects, which were consistent with our results, despite different methods of quantification. However, the relative content for Ce³⁺ ions ([Ce³⁺]_{XPS}) decreased with the doping of Y³⁺ in the report [44], and the authors attributed this to the substitution of Y³⁺ for Ce³⁺.

Table 2. Recent literature on the lattice parameters, $[Ce^{3+}]_{XPS}$, $[V_O]_{XPS}$, and $[V_O]_{Raman}$ of undoped and Y-doped CeO₂.

Authors	Lattice Parameters (Å)	[Ce ³⁺] _{XPS} (%)	[V _O] _{XPS} (%)	$[V_{O}]_{Raman}$
Xu et al. [41]	5.4178 (CeO ₂);	12.60 (CeO ₂);	28.53 (CeO ₂);	1.1 (CeO ₂);
	5.4217 (Y-doped)	21.38 (Y-doped)	33.81 (Y-doped)	4.9 (Y-doped)
Chahal et al. [42]	5.413 (CeO _{2-δ});	26.6% (CeO _{2-δ});	46.9% (CeO _{2-δ});	1.9 (CeO _{2-δ});
	$5.416 (Ce_{0.97}Y_{0.03}O_{2-\delta})$	35.3% (Ce _{0.97} Y _{0.03} O _{2-δ})	52.6% (Ce _{0.97} Y _{0.03} O _{2-δ})	2.9 (Ce _{0.97} Y _{0.03} O _{2-δ})
Yang et al. [43]	5.4129 (CeO ₂);	18.13% (CeO ₂);	/	/
	5.4325 (Y-doped)	22.88% (Y-doped)	/	7
Liyanage et al. [44]	/	11.40 (CeO ₂);	/	/
		$10.07 (Ce_{0.89}Y_{0.11}O_{1.94})$		

OSC is the basic characteristic of CeO_2 and the premise of numerous applications. Therefore, the O₂-TPD experiment was employed to evaluate the OSC of CeO₂. Figure 7 shows the O₂-TPD spectra of the Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂ powders. For the Undoped CeO₂, the asymmetrical peak of either the low temperature at ~170 °C or the high temperature at ~600 °C (light yellow area) implied the existence of at least two kinds of oxygen species at various coordination environments. The oxygen desorption at low temperatures could be attributed to the release of surface/subsurface lattice oxygen, while the oxygen desorption at high temperatures could be ascribed to the release of bulk lattice oxygen, which was consistent with the reported results [45]. Moreover, it could be clearly observed that the oxygen desorption was rapid at the early stages of the process ($120 \sim 170 \circ C$), suggesting that there were large amounts of adsorbed oxygen on CeO_2 , which could emigrate quickly at low temperatures. After the temperature reached ~170 °C, the oxygen desorption started to decrease quickly until a temperature of ~350 °C was reached, and then basically maintained a steady release of oxygen until \sim 570 °C. Subsequently, the Undoped CeO₂ experienced the second oxygen release from 570 to 820 °C. Remarkably, the O₂-TPD curve coincided with the baseline after 820 °C, suggesting that there was little release of oxygen for Undoped CeO₂ after 820 $^{\circ}$ C. For the H-Y-doped CeO₂, the O₂-TPD profile was similar to that of the Undoped CeO₂. However, the desorption bands at high temperatures occurred at higher temperatures, indicating that the partial substitution of Ce^{4+} ions (0.97 Å) with the large Y ions (1.02 Å) improved the stability of the CeO₂ lattice. For the O₂-TPD profiles of I-Y- and H/I-Y-doped CeO₂, the asymmetrical peak at high temperatures was displaced by a smooth descent peak, indicating that the oxygen desorption mainly occurred on the surface and subsurface of the I-Y- and H/I-Y-doped CeO₂ samples. Furthermore, for the O_2 -TPD profiles of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ after 820 °C, there were still some distances to the baseline (light green area), indicating sustaining oxygen desorption, which could be attributed to the formation of extrinsic V_O defects in the interior of the CeO₂ lattice caused by Y-doping.



Figure 7. O₂-TPD profiles of Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂ powders.

For comparison purposes, the OSC was quantified by the amount of O₂ desorption per gram of CeO₂ sample by measuring the corresponding peak areas of O₂-TPD profiles. The quantified OSC values (labeled as [OSC]) of the Undoped and H-Y-, I-Y-, and H/I-Y-doped CeO₂ in the full temperature range are shown in Table 1. Compared with the OSC value of the Undoped CeO₂, all of the Y-doped CeO₂ samples were enhanced, and the sequence of [OSC] was as follows: H-Y-doped CeO₂ (0.372 mmol/g) > H/I-Y-doped CeO₂ (0.353 mmol/g) > I-Y-doped CeO₂ (0.248 mmol/g) > Undoped CeO₂ (0.153 mmol/g). The OSC of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ were increased by 143.1%, 62.1%, and 130.7%, respectively, compared with that of the Undoped CeO₂. The enhanced OSC of all the Y-doped CeO₂ could be explained as follows: when Y³⁺ ions were doped into the CeO₂ lattice to substitute Ce⁴⁺ ions, the extrinsic V_O defects were formed to keep the electric neutrality of their fluorite structure, accompanied by the increase in the number of oxidation/reduction cycles composed of Ce³⁺ and Ce⁴⁺ states (Ce³⁺↔Ce⁴⁺). Y-doping of CeO₂ possesses both intrinsic and extrinsic V_O defects, as well as the oxidation/reduction cycle of Ce³⁺ \leftrightarrow Ce⁴⁺, which could determine the transfer of oxygen ions and OSC.

4. Conclusions

In summary, three various routes were adopted to successfully synthesize Y-doped CeO_2 solid solutions. The large Y cations were incorporated into the CeO_2 lattice with normal trivalence and formed a Y-doped CeO_2 solid solution while holding the cubic fluorite structure of CeO₂. The results of O 1s XPS and Raman spectroscopy indicated that pure CeO₂ crystal itself contained a certain number of intrinsic V_O defects. With the substitution of Ce^{4+} ions with Y^{3+} ions in the CeO_2 lattice, local lattice expansion of CeO₂ crystal occurred, extrinsic $V_{\rm O}$ defects were formed, and there was an increase in the number of oxidation/reduction cycles composed of Ce³⁺ and Ce⁴⁺ states. Moreover, the relative concentrations of $V_{\rm O}$ defects were quantified by the A_{592}/A_{464} values obtained from Raman spectra, which were 1.47, 0.93, and 1.16 for the H-Y-, I-Y-, and H/I-Y-doped CeO_2 , respectively, and were higher than that of the undoped one (0.67). There were large amounts of adsorbed oxygen on CeO₂, which could emigrate quickly at low temperatures, and the OSCs of the H-Y-, I-Y-, and H/I-Y-doped CeO₂ were increased by 143.1%, 62.1%, and 130.7%, respectively, compared with that of the Undoped CeO₂ (0.153 mmol O_2/g CeO_2). Both the intrinsic and extrinsic V_O defects, as well as the oxidation/reduction cycle of $Ce^{3+} \leftrightarrow Ce^{4+}$, could determine the enhanced OSC of Y-doped CeO₂. The CeO₂ with doping during only the hydrothermal process exhibited the maximum values of OSC, suggesting the effectiveness of the doping.

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