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Authors

Youn, Jae-Rang

Ding, Honghe

Xia, Yujian

et al.

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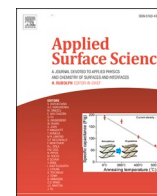
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Full Length Article

A comparative study on cubic and tetragonal Ce-ZrO₂ supported Rh catalysts for N₂O decompositionJae-Rang Youn^a, Honghe Ding^{b,c}, Yujian Xia^b, Jorge Moncada^d, Roberto Colina-Ruiz^e, Jinghua Guo^{b,c,*}, Min-Jae Kim^{a,b,*}^a Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, South Korea^b Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA^c Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA^d National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA^e Center for Advanced Radiation Sources, The University of Chicago, Chicago, IL 60637, USA

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ABSTRACT

Zirconium oxide (ZrO₂) exhibits strong synergy with cerium oxide (CeO₂), acting as a structural and electronic promoter during catalytic redox reactions. As a result, Ce-ZrO₂ composite oxides are widely used as supports in various catalytic systems. In our previous work, we demonstrated that the incorporation of Zr⁴⁺ into the CeO₂ lattice significantly enhanced Rh dispersion, improved redox ability, and stabilized surface Rh species, which collectively boosted the de-N₂O activity of Rh/Ce-ZrO₂ catalysts. Building on these findings, the present study emphasizes that the crystallographic phase of Ce-ZrO₂, governed by the Ce/Zr ratio, plays a decisive role in tuning the physicochemical environment of Rh active sites and thereby optimizing catalytic performance. Tailoring the Ce/Zr ratio to favor the cubic fluorite structure emerges as a promising strategy for the rational design of highly active and stable catalysts for N₂O decomposition and potentially other redox-sensitive environmental applications.

1. Introduction

For a long time, nitrous oxide (N₂O) has been considered as a harmless gas [1,2]. In recent years, however, N₂O has been identified as a strong contributor to the greenhouse effect since the global warming potential of N₂O is 310 times higher than that of CO₂ [1,2]. In addition, the atmospheric concentration of N₂O has been increasing at an annual rate of 0.2 % per year due to natural and human activity [1,2]. In terms of anthropogenic, there are two major techniques that can be applied to control the amount of N₂O emitted at point sources; the selective catalytic reduction (SCR) and catalytic decomposition. The SCR shows high activity at low temperatures and employs a reductant such as hydrocarbon or ammonia, but the use of a reducing agent makes this technique more expensive and less attractive than others [2,3]. In contrast, catalytic decomposition (2N₂O → 2 N₂ + O₂) is a very simple and cost-effective method. However, the commercial N₂O decomposition catalysts are generally operated at relatively high temperatures, particularly under practical exhaust conditions where O₂ and H₂O are present, as

reported in the literature [3]. Therefore, there is a pressing need for the development of catalysts capable of achieving high activity at lower temperatures and many attempts have been made to develop active catalysts for N₂O decomposition, including noble metals, pure and mixed oxides, and ion-exchanged zeolites [1–3].

Cerium oxide (CeO₂) supported Rh catalysts have received much interest due to their high activity for N₂O decomposition at low temperature (below 400 °C) [4,5]. This is largely attributed to the excellent oxygen storage capacity and redox properties of CeO₂, as well as its ability to stabilize dispersed Rh particles [4–7]. However, Rh/CeO₂ catalyst still does not have enough catalytic performance for industrial application, and it can be significantly deteriorated in the presence of inhibition gases such as oxygen, water vapor, and nitric oxide [7]. For this reason, researchers have attempted to overcome this drawback of Rh/CeO₂ catalyst. According to literature, CeO₂-based support partially substituted by Pr, La, and Zr was reported to improve the catalytic activity in the presence of inhibition gas via changing physical and chemical properties of the catalyst [4]. In particular, the partial

* Corresponding authors at: Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, South Korea and Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

E-mail addresses: jguo@lbl.gov (J. Guo), mkim@kier.re.kr (M.-J. Kim).

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replacement of CeO_2 by ZrO_2 was known to improve the redox properties and metal dispersion owing to the formation of a solid solution [4,7]. In our previous report, we prepared a series of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ -supported Rh catalysts, and their catalytic activity for N_2O decomposition was tested in the 200–400 °C temperature range [7]. It has been demonstrated that partial substitution of Ce^{4+} with Zr^{4+} in the CeO_2 lattice improves Rh dispersion and catalytic activity [7]. These improvements were primarily attributed to changes in surface area and oxygen mobility. However, not all Rh/Ce-Zr O_2 catalysts exhibited improved activity, and those with lower ZrO_2 content consistently showed superior catalytic performance compared to the Rh/Ce-Zr O_2 catalysts with higher ZrO_2 content [7]. This indicated that the Ce/Zr ratio is important for the catalytic efficiency of N_2O decomposition.

Many researchers have reported the influence of the Ce/Zr ratio on catalytic performance [4]. Ce-rich compositions typically form a cubic fluorite-type structure, whereas Zr-rich compositions tend to adopt a tetragonal phase [8]. These distinct structural forms not only exhibit different thermodynamic stabilities but also significantly influence key properties such as oxygen vacancy formation, lattice oxygen mobility, and metal-support interactions. In particular, the cubic phase has been associated with enhanced oxygen storage and redox cycling, which are highly relevant to N_2O decomposition mechanisms. Nevertheless, the specific influence of the crystallographic structure of the support on metal dispersion, surface activity, and overall catalytic behavior remains insufficiently understood. Therefore, more detailed information about the structure-activity relationship is essential for a better understanding of the catalyst system. In this study, we aim to elucidate the structure-activity relationship of Rh/Ce-Zr O_2 catalysts in N_2O decomposition by focusing on the crystallographic phase of the Ce-Zr O_2 support. To this end, two representative Ce/Zr compositions were selected: $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$, which exhibit cubic and tetragonal phases, respectively. Although both catalysts contain the same Rh loading, they are significantly different in terms of Rh particle dispersion, redox behavior, and surface activity. By employing a combination of physicochemical characterization techniques, including XRD, H_2 -TPR, XANES/EXAFS, XPS, and *in-situ* FT-IR spectroscopy, we systematically compare how the structural symmetry of the support influences the distribution and chemical state of Rh species, oxygen mobility, and intermediate surface reactions.

2. Experimental

2.1. Catalysts preparation

$\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ supports were synthesized by the co-precipitation method [7,9]. Stoichiometric quantities of cerium nitrate (99 %, Aldrich) and zirconium oxynitrate (99 %, Aldrich) were dissolved in distilled water. The 15 wt% KOH solution was slowly added dropwise (2 mL/min) with constant stirring solution until the pH of the solution was 10.1, and the slurry was aged for 3 h at room temperature. The precipitate was thoroughly washed several times with distilled water, air-dried at 110 °C for 24 h, and then pre-calcined at 550 °C for 4 h under ambient air condition. Rh/ $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and Rh/ $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalysts were synthesized by an incipient wetness impregnation method with Rh (NO_3) solution (nominal amount of Rh: 1 wt%) [7,9]. The prepared catalysts were air-dried at 110 °C for 24 h and calcined at 550 °C for 4 h.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-2500 diffractometer in a 2θ range of 10 – 90 ° ($\text{Cu K}\alpha$ radiation, 40 kV, 200 mA). Synchrotron micro X-ray diffraction (μXRD) measurements were carried out at the 4-BM beamline of the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory (BNL) in Upton, NY, USA. A monochromatic X-ray beam of 18000 eV and a dwell time of 60 s was used to achieve high-resolution diffraction patterns in

transmission mode using a Perkin-Elmer 1621 AN/CN amorphous silicon flat-panel X-ray detector. Powdered catalyst samples were placed onto Kapton double tape to minimize preferred orientation effects. The Brunauer-Emmett-Teller (BET) specific surface area of the calcined catalysts was estimated by N_2 physisorption technique using a BELSORP-max (BEL Japan, Inc). Before analysis, the samples were pretreated under vacuum at 200 °C for 24 h to eliminate residual surface impurities. The sorption amount of N_2O on the as-prepared samples was estimated by thermogravimetric analysis (TGA, TA instruments, SDT-Q600). Prior to N_2O sorption analysis, a sample was pretreated at 400 °C for 1 h under N_2 flow to remove any impurities and then cooled down to 50 °C. The weight change was recorded under a flow of 0.5 % N_2O in He balance until saturation. H_2 temperature-programmed reduction (H_2 -TPR) and O_2 temperature-programmed desorption (O_2 -TPD) experiments were carried out on an Autochem II 2920 (Micromeritics) equipped with a thermal conductivity detector (TCD). A sample (100 mg) was pretreated at 400 °C in a flow of 10 % O_2 in He balance for 1 h. Afterward, H_2 -TPR was conducted under 10 % H_2 in Ar balance with heating from 50 to 800 °C at a rate of 5 °C min^{-1} . For O_2 -TPD, a sample (200 mg) was pretreated at 400 °C in He flow for 1 h. After cooling to a temperature below 50 °C, O_2 -TPD was performed under He flow from 50 to 700 °C at a ramping rate of 5 °C min^{-1} . Rh dispersion in the samples was observed by CO pulse chemisorption using an Autochem II 2920 (Micromeritics), assuming an adsorption stoichiometry of one CO per Rh surface atom ($\text{CO/Rh} = 1$) [7]. Prior to each analysis, the sample was reduced at 400 °C for 1 h in 10 % H_2 in Ar flow. Rh K-edge XANES/EXAFS and Ce L_3 -edge XANES measurements were collected at 8-ID (ISS) and 4-BM (XFM) beamlines of the NSLS-II in BNL, respectively. ISS beamline has a damping wiggler source that provides high flux photon (10^{14} photon per second at 10 keV at full accelerator current) with a 1 mm $\times$ 1 mm spot size. The beamline has a high heat load Si (111) monochromator with a resolution of $\sim 1 \times 10^{-4}$ of the incident energy [10]. A total fluorescence yield detector (PIPS diode) and series of ion chambers were used as fluorescence and transmission mode detectors, respectively. At XFM, the incoming photon flux energy was tuned with a cryo-cooled Si (111) double crystal monochromator, with an energy resolution of ~ 0.2 eV at the Ce L_3 -edge and a beam size of ~ 0.5 mm 2 . Data were collected in fluorescence mode using a 7-element Canberra/Mirion Si drift detector coupled with Xspress3 electronics. Powder samples for XFM experiment were prepared by dusting a few milligrams onto Kapton double tape. Energy calibration was performed with Rh foil for the Rh K-edge ($\sim 23,220$ eV) and CeO_2 standards for the Ce L_3 -edge ($\sim 5,723$ eV). Data processing, including dead-time correction, pre-edge subtraction, and post-edge normalization to the incident intensity (I_0), was carried out using the Larch XAS viewer software, and the EXAFS $\chi(k)$ functions were extracted and k^2 -weighted before Fourier transformation over the k -range of 3.0–12.0 $\text{\AA}^{-1}$ [11]. To estimate the oxidation state from the Ce L_3 -edge spectrum, XANES fitting was further conducted using the Athena software, where curve-fitting was performed after subtraction of an arctangent background function [12]. Soft X-ray absorption spectroscopy (sXAS) experiments for O K-edge was carried out on the beamline 7.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. O K-edge spectra were observed using both total electron yield (TEY) and total fluorescence yield (TFY). All TEY and TFY spectra were normalized by the incident beam flux, obtained using the up-stream gold mesh. The energy position of O K-edge was calibrated by the reference sample, with 0.2 eV resolution. X-ray photoelectron spectroscopy (XPS) was conducted in an ESCALAB Mark II spectrometer (Vacuum Generators, UK) using Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). The binding energy (E_B) was corrected using the adventitious carbon (C 1s) peak at 285.0 eV. *In-situ* FT-IR analysis was carried out in a porous ceramic reaction cell with ZnSe window, using a PIKE technologies diffuse reflectance IR accessory that was placed in a NICOLET iS10 (Thermo Scientific) spectrometer equipped with an MCT-A detector working at liquid N_2 temperature. The spectra were recorded by using 64 accumulating scans, which was depicted in

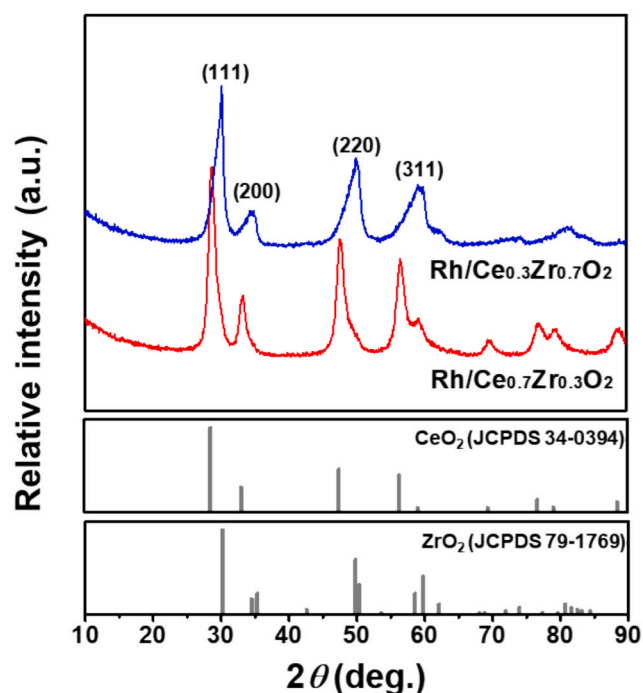


Fig. 1. X-ray diffraction patterns of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts.

absorbance unit at a resolution of 8 cm⁻¹. Before the *in-situ* FT-IR experiment, the catalysts were pretreated under He gas flow at 400 °C for 1 h to remove any impurities, then cooled to 25 °C. A gas mixture of 500 ppm N₂O in He was introduced into the reaction cell to observe N₂O adsorption on the sample, followed by heating the sample to 400 °C under He flow.

2.3. Catalytic reaction

Catalytic activity for N₂O decomposition was carried out in a fixed-bed tubular reactor under atmospheric pressure. The reaction temperature was controlled with a K-type thermocouple, which is directly inserted into the catalyst bed. Prior to each test, the catalyst was exposed by a gas stream of 10 % O₂/N₂ for pretreatment. The simulated gas was introduced into reactor; The gas composition: 500 ppm N₂O, 500 ppm N₂O + 3 % O₂, 500 ppm N₂O + 3 % H₂O, 500 ppm N₂O + 3 % O₂ + 3 % H₂O, and 500 ppm N₂O + 500 ppm NO in N₂ balance. Gas hourly space velocity (GHSV) was 45,000 h⁻¹. Effluent gas from the reactor was analyzed on-line using an infrared gas analyzer (Madur Polska, Sensonic IR-1).

$$N_2O_{conversion}(\%) = \frac{[N_2O]_{out} - [N_2O]_{in}}{[N_2O]_{in}}$$

3. Results and discussion

3.1. Catalysis characterization

XRD analysis was performed to investigate the crystal structure of

Rh-supported Ce-ZrO₂ mixed oxides in the whole compositional range, given in Fig. S1. All the observed peaks of Rh/CeO₂ and Rh/ZrO₂ catalysts are identified to cubic fluorite oxide-type structure of CeO₂ (Fm3m space group, JCPDS #34-0394) and tetragonal in major (P4₂/nmc space group, JCPDS #79-1769) with two minor monoclinic peaks (P2₁/c space group, JCPDS #37-1484) at 2θ = 28.2° and 31.2°, respectively [7–9]. In the patterns for the Rh-supported Ce-ZrO₂ composite oxides with intermediate compositions, the loss of symmetry, which entails the transition from the cubic fluorite structure to the tetragonal structure of zirconia is recorded (Fig. S1). Fig. 1 presents the XRD patterns of two representative Rh-supported Ce-ZrO₂ catalysts with different Ce/Zr ratios, Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂, aimed in this study. The XRD pattern of Rh/Ce_{0.3}Zr_{0.7}O₂ exhibited peaks similar to those of the cubic Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst, without any additional peaks. However, all reflection peaks in Rh/Ce_{0.3}Zr_{0.7}O₂ were shifted toward higher diffraction angles, indicating a decrease in interplanar spacing and lattice constants, likely due to the substitution of Ce⁴⁺ ions by the smaller Zr⁴⁺ ions in the lattice [7,14]. These results show that the Ce/Zr ratio plays a critical role in determining the crystal structure of Rh/Ce-ZrO₂ catalysts, even when synthesized using identical methods. Furthermore, the characteristic peaks of Rh/Ce_{0.3}Zr_{0.7}O₂ were notably broad and asymmetric at 30.1°, 34.6°, 50.1°, and 59.4°. This suggests that the structure can be interpreted as a poorly crystallized cubic, tetragonal phase, or multiple phases. This ambiguity hinders the clear identification of the crystal structure in our synthesized samples. Escibano et al. insisted the small crystallite size of Ce-ZrO₂ composite oxides as the primary reason for the broad and asymmetric peaks observed in their XRD patterns [15]. They also noted that, due to this small crystallite size, conventional powder X-ray diffraction techniques have limitations in clearly distinguishing between cubic and tetragonal phases in Ce-ZrO₂ composite oxides samples [15]. Using the Scherrer equation, we determined the crystallite sizes of our samples to be 6.6 nm for Rh/Ce_{0.7}Zr_{0.3}O₂ and 5.4 nm for Rh/Ce_{0.3}Zr_{0.7}O₂, confirming that both possess very small crystallite dimensions (Table 1). These results are consistent with the findings of Escibano et al. and further reinforce the notion that conventional powder X-ray diffraction methods have intrinsic limitations in clearly distinguishing between cubic and tetragonal phases in Ce-ZrO₂ composite oxide samples with such small crystallite sizes [15]. Therefore, it is necessary to employ more precise and advanced analytical techniques to accurately determine their structural phases. The crystal structures of the prepared samples, Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂, were re-examined using synchrotron-based micro X-ray diffraction to clearly identify their crystallographic phases, increasing spatial resolution and beam flux, as shown in Fig. 2(a). The synchrotron-based μXRD results revealed distinct differences compared to those obtained from conventional XRD measurements. This was particularly observed in the Rh/Ce_{0.3}Zr_{0.7}O₂ sample, where the synchrotron data clearly confirmed the presence of a well-defined tetragonal structure, with no XRD patterns of cubic fluorite-phase. All the observed peaks of Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst are identified to cubic structure (Fig. 2(b)), having symmetrical one peak as (400), while those of Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst are indexed to tetragonal structure which has two peaks clearly splitting of (400) and (004) plane, indicating c/a > 1 (Fig. 2(c) and an inset of Fig. 2(a)) [7]. In addition, a transition from the cubic fluorite phase to the tetragonal zirconia structure is typically accompanied by a reduction in symmetry, leading to peak splitting in the XRD pattern. For instance, the cubic (200)_c reflection at 14.6° divides into the (002)_t and

Table 1
Characteristics of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts.

Catalysts	Surface area (m ² g ⁻¹)	Total pore volume (m ³ g ⁻¹)	Crystallite size* (nm)	Lattice parameter (Å)	N ₂ O sorption uptake at 50 °C** (mmol g ⁻¹)
Rh/Ce _{0.7} Zr _{0.3} O ₂	78.2	0.081	6.6	5.6868	8.7x10 ⁻⁵
Rh/Ce _{0.3} Zr _{0.7} O ₂	20.7	0.015	5.4	5.1333	2.4x10 ⁻⁵

* Calculated by XRD.

** Calculated by TGA analysis.

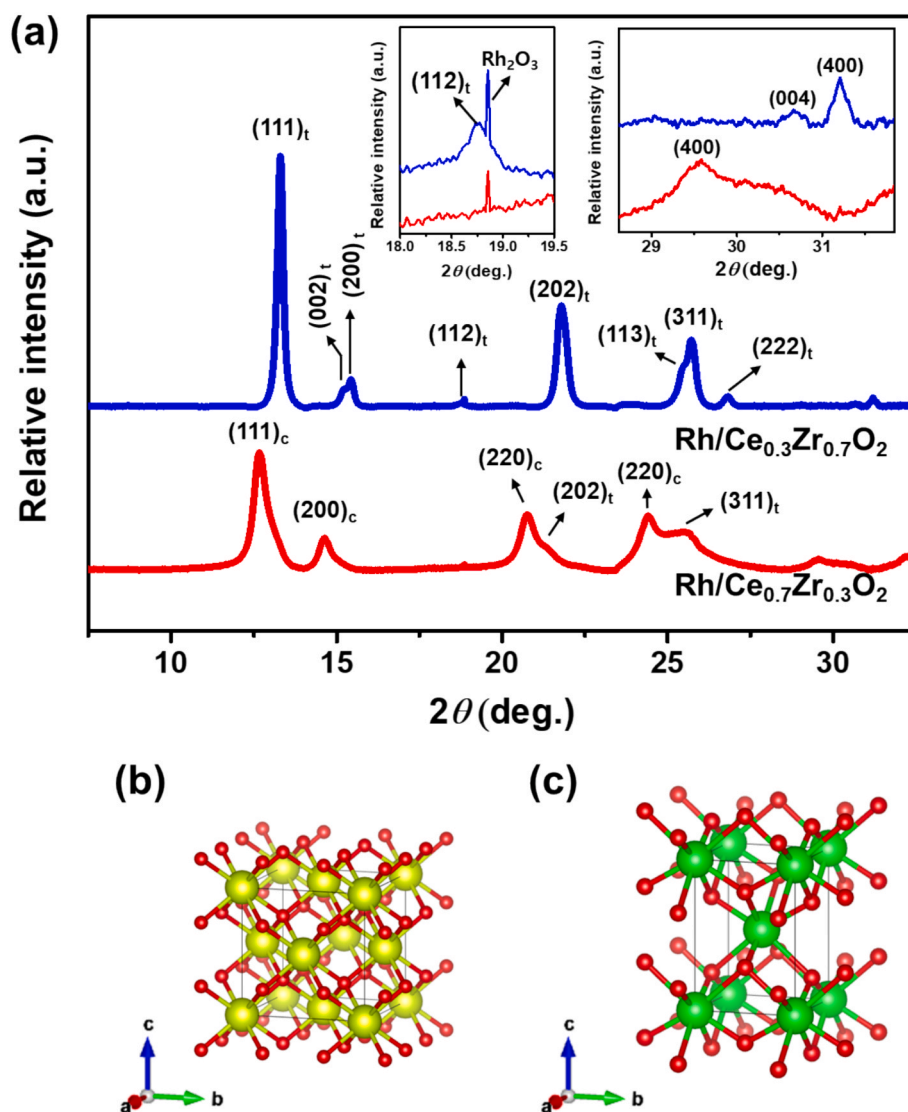


Fig. 2. Synchrotron X-ray diffraction patterns of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts with an inset in the region of the (400) and (004) peaks (a), cubic fluorite oxide-type structure of pure CeO₂ (b), and tetragonal oxide-type structure of pure ZrO₂ (c).

Table 2

CO chemisorption of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts.

Catalysts	Rh dispersion (%)	Rh surface area (m ² g ⁻¹)	Rh crystallite size (nm)
Rh/Ce _{0.7} Zr _{0.3} O ₂	46.7	3.7	1.5
Rh/Ce _{0.3} Zr _{0.7} O ₂	9.2	0.8	8.9

(110)_t reflections in the tetragonal phase, appearing around $2\theta \approx 15.3^\circ$ using synchrotron X-ray radiation [15]. Interestingly, diffraction peaks associated with Rh oxide phases were not observed in either of the two samples using lab-based XRD, likely due to the low Rh content, ultrafine particle size, and high dispersion across the support. However, synchrotron-based μ XRD revealed a small but detectable Rh oxide-related peak at 18.8° because of the increment on the spatial resolution. To further evaluate the particle size and dispersion of Rh nanoparticles, CO chemisorption analysis was conducted, and the detailed results are summarized in Table 2. Based on these results, we clearly confirmed that the samples under investigation exhibit either cubic or tetragonal structures depending on the Ce/Zr ratio.

Table 1 summarizes the textural properties of the catalysts. The BET surface area of the Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst ($78.2 \text{ m}^2 \text{ g}^{-1}$) is much higher than that of the Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst ($20.7 \text{ m}^2 \text{ g}^{-1}$). Additionally, the total pore volume of the Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst is almost five times higher than that of the Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst, and the crystallite size of the tetragonal Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst is smaller than that of the cubic Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst. This indicates that the surface area and pore volume can change depending on the crystal structure of the catalyst. The lattice parameters were measured assuming a cubic cell system and are in good agreement with those calculated by Kalamaras et al., with the value for Rh/Ce_{0.3}Zr_{0.7}O₂ being closer to that of tetragonal ZrO₂ ($5.1272 \text{ \AA}$), suggesting shrinkage of the Ce-O-Zr crystal lattice due to the insertion of Zr⁴⁺ ions into the CeO₂ lattice [13]. This is consistent with the fact that the ionic radius of Zr⁴⁺ ($0.84 \text{ \AA}$) is smaller than that of Ce⁴⁺ ($0.97 \text{ \AA}$), resulting in a decreased lattice parameter for the tetragonal Rh/Ce_{0.3}Zr_{0.7}O₂ [7,16]. CO chemisorption analysis (Table 2) revealed that the cubic Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst exhibited a markedly higher Rh dispersion (46.7 %) and larger Rh surface area ($3.7 \text{ m}^2 \text{ g}^{-1}$) compared to the tetragonal Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst, which showed only 9.2 % dispersion and $0.8 \text{ m}^2 \text{ g}^{-1}$ surface area. The Rh crystallite size estimated from CO uptake was significantly smaller for the cubic catalyst (1.4 nm) than for the tetragonal catalyst (8.7 nm),

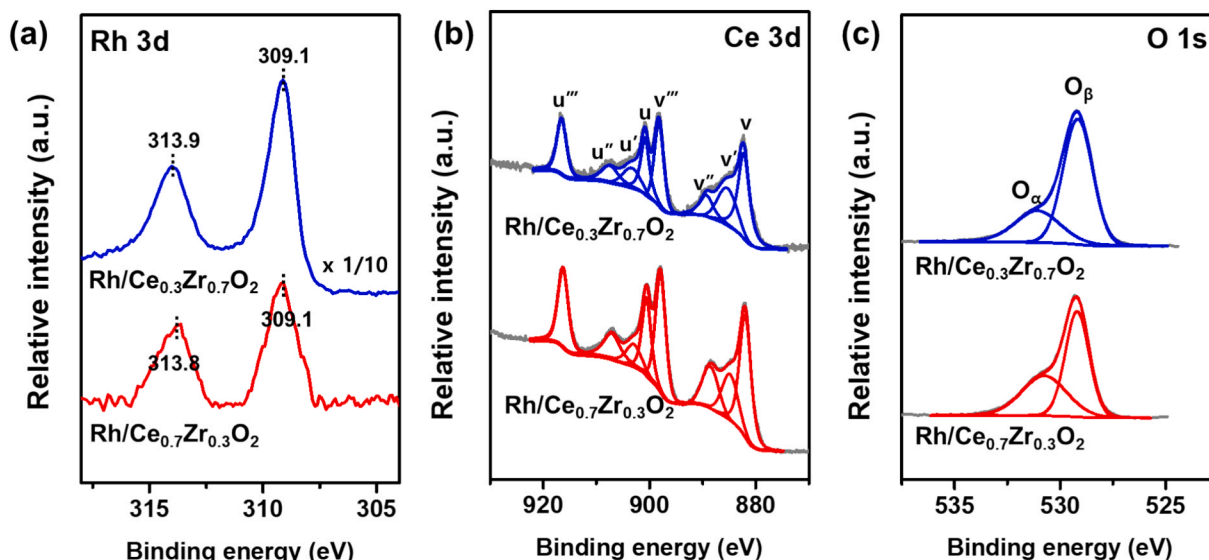


Fig. 3. XPS spectra of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂; Rh 3d (a), Ce 3d (b), and O 1s (c).

Table 3

Comparison of Ce³⁺ content and defect oxygen concentration in Rh/Ce-ZrO₂ from XPS and Ce L₃-edge XANES analysis.

Catalysts	Relative concentration of Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺) ^a (%)	Absolute concentration Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺) ^a (%)	Relative concentration of O _α /(O _α +O _β) ^b (%)	Ce ³⁺ fraction ^c (%)
Rh/ Ce _{0.7} Zr _{0.3} O ₂	18.3	12.8	43.2	20.5
Rh/ Ce _{0.3} Zr _{0.7} O ₂	16.0	4.8	29.4	13.1

^a Estimated by Ce 3d XPS.

^b Estimated by O 1s XPS.

^c Estimated by Ce L₃-edge XANES.

indicating that the cubic Ce-ZrO₂ support provides a more favorable environment for dispersing Rh nanoparticles and stabilizing them against agglomeration. These structural advantages are expected to contribute directly to the enhanced catalytic performance of the cubic Rh/Ce-ZrO₂ catalyst in N₂O decomposition.

XPS was performed to examine the oxidation states and binding energies of Rh, Ce, and O species in Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts. Spectral deconvolution was conducted following the subtraction of a Shirley-type background, using a combination of Gaussian and Lorentzian functions. The Rh 3d core-level spectra are presented in Fig. 3(a). Although the spectrum of Rh/Ce_{0.7}Zr_{0.3}O₂ exhibited noticeable noise due to the small Rh particle size (1.7 nm), Rh 3d_{5/2} and Rh 3d_{3/2} peaks were observed at 309.1 eV and 313.8 eV, respectively, in both catalysts [7,16]. These binding energies are consistent with values reported for Rh³⁺ species in the literature, suggesting that Rh is predominantly present in the +3 oxidation state on the surface, regardless of support structure or Rh particle size [7,16]. Fig. 3(b) displays the Ce 3d XPS spectra of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts. The spectral features labeled *v* and *u* correspond to the Ce 3d_{5/2} and Ce 3d_{3/2} spin-orbit components, respectively [17–19]. The *v* series comprises peaks at 882.1, 885.0, 888.6, and 897.9 eV, while the *u* series includes peaks at 900.5, 903.0, 907.1, 908.1, and 916.3 eV [16–18]. Among these, the peaks denoted as *v'* and *u'* are associated with Ce³⁺ species characteristic of Ce₂O₃, whereas the remaining peaks (*v*, *v''*, *v'''*, *u*, *u''*, and *u'''*) correspond to Ce⁴⁺ states typical of CeO₂ [17–19]. A minor variation in the relative intensities of these peaks was observed between the two catalysts, suggesting that differences in support structure influence the electronic environment of cerium, potentially through charge imbalance effects within the Ce-ZrO₂ lattice. The charge imbalance on CeO₂ induced by the support structure

was investigated by estimating the relative concentrations of Ce³⁺ (Table 3). The relative concentrations were estimated by peak fitting and using the areas under the fitted sections. For a better understanding of the Ce 3d spectra, reference data of pure CeO₂ and Rh/CeO₂ samples were given in Fig. S4. The Ce³⁺ content in pure CeO₂ was estimated to be 14.3 % (±0.14 %), whereas the Rh/CeO₂ sample containing 1 wt% Rh exhibited a slightly increased Ce³⁺ concentration of 15.2 % (±0.21 %). This phenomenon is well-matched with the study reported by Rico-Pérez et al., who demonstrated that in RhO_x/CeO₂ catalysts, charge transfer from Rh to CeO₂ leads to the generation of oxygen vacancies and improved oxygen mobility [5]. They found that Rh³⁺ species strongly interact with Ce⁴⁺ sites, promoting localized electron interaction and enhancing catalytic activity [5,7]. In this study, XPS analysis revealed that the Ce³⁺ content in Rh/Ce_{0.7}Zr_{0.3}O₂ was 18.3 %, while Rh/Ce_{0.3}Zr_{0.7}O₂ exhibited a Ce³⁺ concentration of 16.0 %, as summarized in Table 3. Both catalysts showed higher Ce³⁺ content compared to pure CeO₂ and Rh/CeO₂ (Fig. S4). The O 1s spectra of the samples are plotted in Fig. 3(c). Both catalysts exhibited two well-defined peaks in the O 1s spectra located at around 529.1 and 530.7 eV [17–19]. The one at 529.1 eV was ascribed to the lattice oxygen (O_β), and the other observed at 530.7 eV was attributed to defect-oxygen species (O_α) [17–19]. The concentration of defect oxygen in the Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst was estimated to be 27 %, which is notably higher than the 21 % observed in the Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst. Defect oxygen is known to enhance oxygen mobility on the catalyst surface and contributes to improved metal dispersion by providing anchoring sites on the surface [7]. Moreover, the formation of an electric double layer [O^{δ-} and O^{δ+}] at the metal-support interface, particularly around Rh nanoparticles, strengthens metal-support interactions and promotes superior catalytic activity through increased oxygen lability and reducibility [7]. It reveals that the

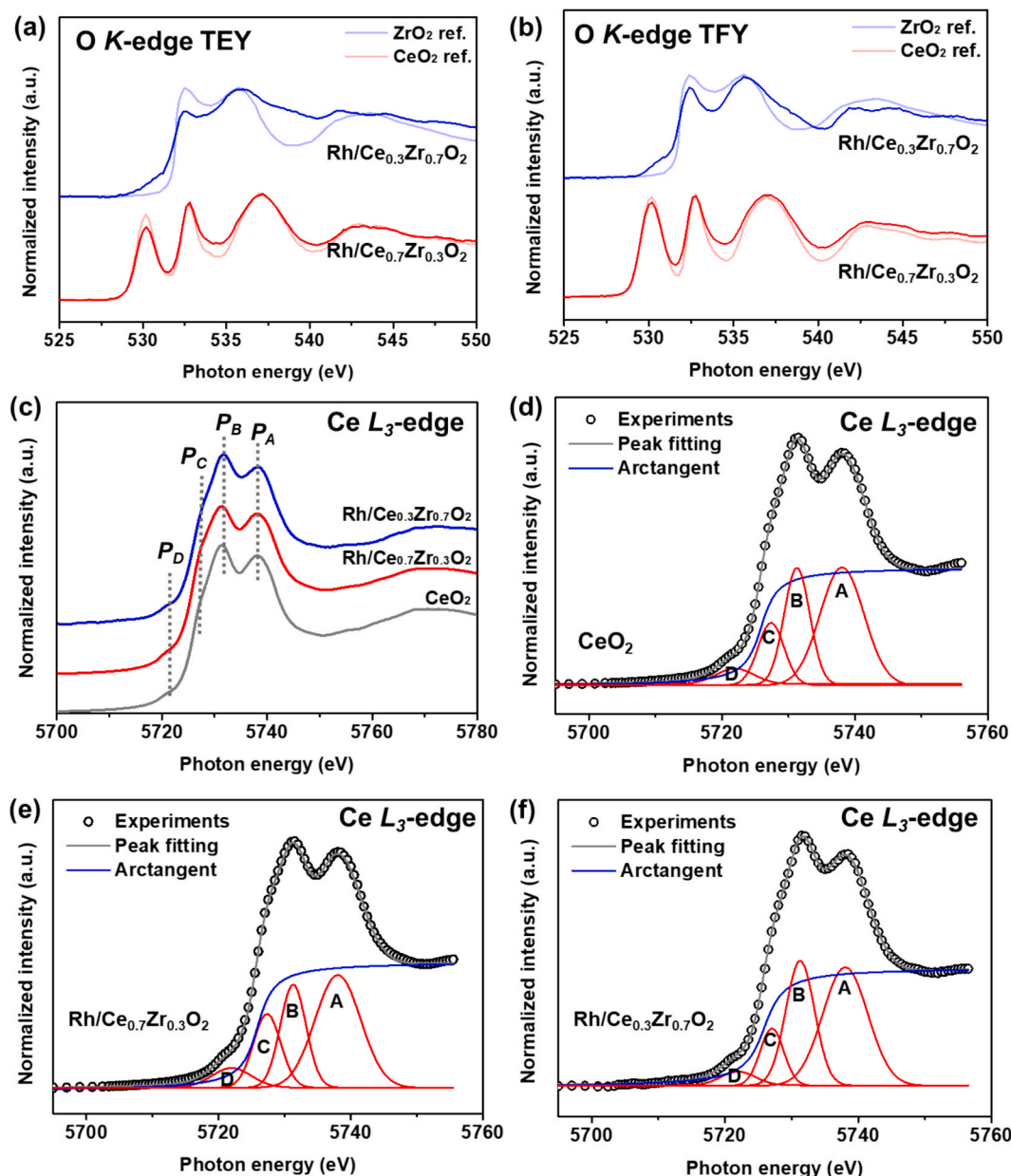


Fig. 4. Normalized O *K*-edge of the Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts using the (a) total electron yield (TEY) and (b) total fluorescence yield (TFY) mode. Normalized Ce *L*₃-edge XAS spectra (c) and Ce *L*₃-edge XAS spectra fitting results of the CeO₂ (d), Rh/Ce_{0.7}Zr_{0.3}O₂ (e), and Rh/Ce_{0.3}Zr_{0.7}O₂ (f) catalysts.

surface electronic properties of the catalyst components are significantly influenced by the crystal structure of the Ce-ZrO₂ support.

Soft X-ray absorption spectroscopy (XAS) at the O *K*-edge was performed to investigate how these compositional changes influence the electronic structure and metal-oxygen hybridization. It was recorded using both total electron yield (TEY) with a probing depth around 10 nm, and total fluorescence yield (TFY) with a probing depth larger than 100 nm [20,21]. These spectra in Fig. 4(a) and (b) provide insights into the unoccupied density of states, particularly reflecting the hybridization between O 2*p* orbitals and neighboring cation states such as Ce 4*f* and Zr 4*d* [20]. In the case of CeO₂, the Ce⁴⁺ ions have an electronic configuration of [Xe]4*f*⁰5*d*⁰, which implies a complete absence of electrons in both the 4*f* and 5*d* orbitals [20,22]. This electronic structure promotes strong hybridization between O 2*p* and Ce 4*f* states, giving rise to an intense peak at 530.3 eV corresponding to the O 1*s* → O 2*p*-Ce 4*f* transition [20,22]. Moreover, the crystal field splitting of the Ce 5*d* orbitals results in distinct features at 532.8 eV and 537.1 eV, which can be

attributed to transitions into the Ce 5*d* *e_g* and 5*d* *t_{2g}* states, respectively [20,22]. Upon substitution with Zr⁴⁺ (electronic configuration [Kr]4*d*⁰), as in Rh/Ce_{0.7}Zr_{0.3}O₂, the local electronic structure around oxygen atoms is altered. The introduction of Zr into the lattice enables hybridization between O 2*p* orbitals and the unoccupied Zr 4*d* orbitals [20]. As a result, the electron density of O 2*p* states becomes delocalized across both Ce 4*f* and Zr 4*d* states [20]. This redistribution reduces the possibility of the O 1*s* → O 2*p*-Ce 4*f* transition, thereby resulting in a decrease in the peak intensity [20,22]. Therefore, the presence of Zr leads to a delocalization of O 2*p* orbital contributions between Ce and Zr centers, diminishing the spectral feature associated with Ce-centered hybridized states. In the case of pure ZrO₂, the O *K*-edge spectrum of ZrO₂ exhibits two prominent features centered at approximately 532.4 eV and 535.5 eV. These features are assigned to transitions from the O 1*s* core level into unoccupied states that arise from O 2*p*-Zr 4*d* hybridization [20,22]. The lower-energy feature at 532.4 eV corresponds to hybridized states with Zr 4*d* *t_{2g}* state, while the higher-energy peak at 535.5 eV reflects

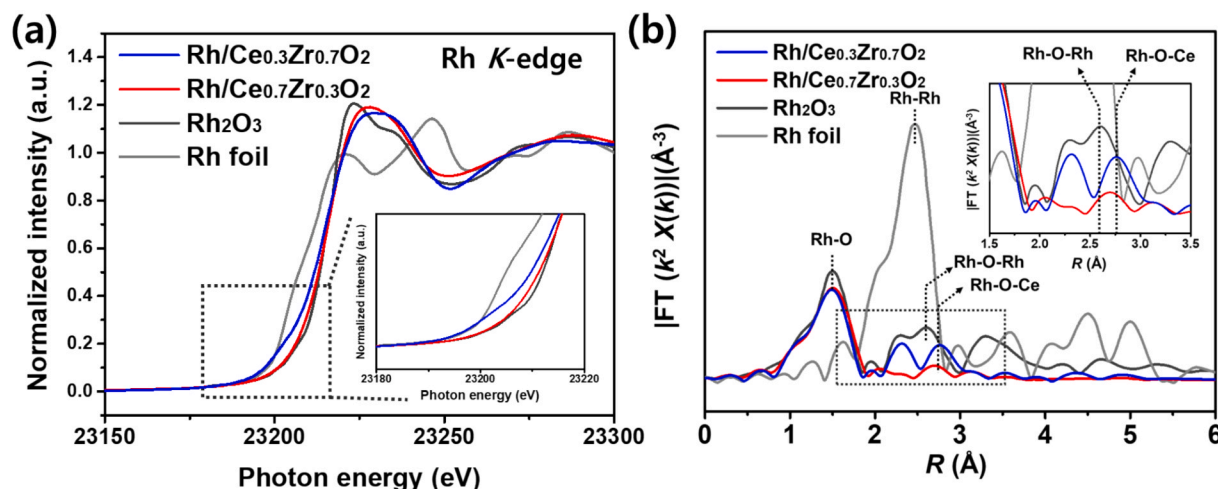


Fig. 5. XANES spectra at the Rh *K*-edge of the Rh catalysts supported over $\text{Ce}_{0.7}\text{Zr}_{0.3}$ and $\text{Ce}_{0.3}\text{Zr}_{0.7}$ (a) and Fourier transform of the k^2 -weighted EXAFS spectra (b). Rh foil and Rh_2O_3 are given as references for comparison.

contributions from Zr 4d e_g state [20,23]. Upon incorporation of Ce^{4+} into the lattice ($\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$), notable spectral changes are observed. A new weak feature appears at 530.3 eV, which is not present in the pure ZrO_2 . This feature is attributed to transitions from O 1s to unoccupied Ce 4f orbitals through O 2p–Ce 4f hybridization [20,22,23]. The 4f⁰ configuration of Ce^{4+} provides possible transition, and their energy position aligns with previously reported Ce–O hybridization features in CeO_2 [20,22,23]. In parallel, the intensity of the main absorption peak at 532.5 eV is reduced in $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$. This reduction indicates a lower overall concentration of Zr and a corresponding decline in the number of O atoms coordinated to Zr sites. Furthermore, the presence of Ce redistributes the unoccupied O 2p-derived states, diminishing the relative contribution of O 2p–Zr 4d hybridization and altering the electronic environment around the oxygen atoms [20,22,23]. When comparing Rh/Ce–ZrO₂ catalysts with cubic and tetragonal phases, partial substitution of Zr^{4+} into cubic CeO_2 or Ce^{4+} into tetragonal ZrO_2 induces notable changes in metal–oxygen hybridization and gives rise to new unoccupied electronic states. These electronic modifications are more pronounced in the TEY spectra, indicating that such effects are enhanced at or near the surface. Given that surface sites are directly involved in catalytic reaction, these surface electronic changes are likely to play a pivotal role in influencing the activity toward N_2O decomposition. To elucidate the electronic structure and oxidation state of cerium in catalysts, Ce *L*₃-edge XAS was performed. Fig. 4(c) presents the normalized Ce *L*₃-edge spectra of CeO_2 , $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$, and $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$. The Ce *L*₃-edge features indicate electronic transitions from Ce 2p_{3/2} core levels to unoccupied Ce 5d states and is highly sensitive to the Ce oxidation state and local coordination environment [24,25]. The Ce *L*₃-edge absorption spectra of CeO_2 and Rh/Ce–ZrO₂ catalysts exhibit four distinct features labeled P_A , P_B , P_C , and P_D (Fig. 4(d–f)). These arise from Ce 2p_{3/2} → 5d transitions involving various final-state configurations, reflecting differences in Ce–O hybridization and crystal field effects [24,25]. The P_A (5738 eV) and P_B (5731.1–5731.8 eV) peaks are related to Ce^{4+} ions in CeO_2 corresponding to a 2p → 4f⁰5d* transition and a 2p → 4f¹5d*L transition [24,25]. Where 2p represents the hole generated at 2p_{3/2}, 5d* indicates the presence of excited electrons at the 5d orbitals, and L represents the ligand hole of the anion orbital [24,25]. The P_C peak (5727.2 eV) is assigned to a combination of crystal-field splitting and excitation of a Ce^{3+} and the P_D feature (5721 eV) is associated with the dipole-forbidden 2p_{3/2} → 4f transition, which is a consequence of a 5d admixture with the 4f state [24,25]. The Ce *L*₃-edge XANES spectra of the investigated samples exhibited the characteristic peaks of both Ce^{3+} and Ce^{4+} states, and the Ce^{4+} oxidation state was dominant. However, a small variation in the intensity of the P_C peak was observed for the Rh/

$\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst, which has a cubic fluorite structure. This spectral variation appears to originate from subtle changes in the local coordination environment, including crystal field splitting, induced by the partial substitution of Zr^{4+} into the CeO_2 lattice. These structural modifications result in changes to the Ce oxidation state. The Ce^{3+} fraction was quantified by calculating the ratio of the integrated area associated with Ce^{3+} to the total area encompassing both Ce^{3+} and Ce^{4+} components (Table 3). As shown in Table 3, this trend is the same as that of the XPS result. The cubic Rh/ $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ sample display a markedly higher Ce^{3+} fraction (20.5 %) than the tetragonal Rh/ $\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ (13.1 %). These results provide insight into the Ce oxidation state and the degree of Ce 4f–O 2p and Ce 5d–O 2p hybridization, which can be changed by the Ce/Zr ratio and local structural environment.

Fig. 5 presents the Rh *K*-edge XANES and EXAFS spectra, offering insights into the local coordination environment and electronic structure of Rh species in the catalysts. As shown in Fig. 5(a), the XANES spectra of the both catalysts closely match that of Rh_2O_3 , indicating that Rh species on the cubic and tetragonal Rh/Ce–ZrO₂ are mainly present in a positive oxidation state ($\text{Rh}^{\delta+}$, $\text{Rh}^0 < \text{Rh}^{\delta+} < \text{Rh}^{3+}$) [26,27]. It is also observed that both the cubic and tetragonal Rh/Ce–ZrO₂ catalysts exhibit absorption edges shifted toward higher energies compared to Rh_2O_3 . This observed shift can be further associated with structural distortions in the Rh coordination environment, which are likely induced by the Jahn–Teller effect [27]. This effect arises when Rh^{3+} ions are incorporated into the oxide lattice, leading to deviations from ideal symmetry and distortion of the first coordination shell. In addition to the main edge features, the pre-edge region (~23,200 eV) reveals a slightly more pronounced peak in the tetragonal Rh/Ce–ZrO₂ catalyst compared to its cubic Rh/Ce–ZrO₂ [26,27]. Since the XPS results show negligible differences in peak position and Rh oxidation state between the two catalysts, the enhanced pre-edge intensity is more likely attributed to a decrease in local symmetry around Rh in the tetragonal structure [26–28]. Such an increase in pre-edge intensity is characteristic of non-centrosymmetric environments, where increased d–p orbital mixing leads to greater dipole-allowed transitions [26,27]. This suggests that Rh species in the tetragonal catalyst experience a more distorted coordination geometry, likely due to the intrinsic anisotropy of the tetragonal Ce–ZrO₂ lattice. These results indicate that the crystal structure of the support has a significant influence not only on the oxidation state but also on the local symmetry of the Rh nanoparticles. Fig. 5(b) shows the Fourier-transformed Rh *K*-edge EXAFS spectra of the catalysts, providing insights into the local coordination structure of Rh species. For both cubic and tetragonal Rh/Ce–ZrO₂ catalysts, a single dominant peak is observed at ~1.6 Å, which corresponds to the Rh–O coordination

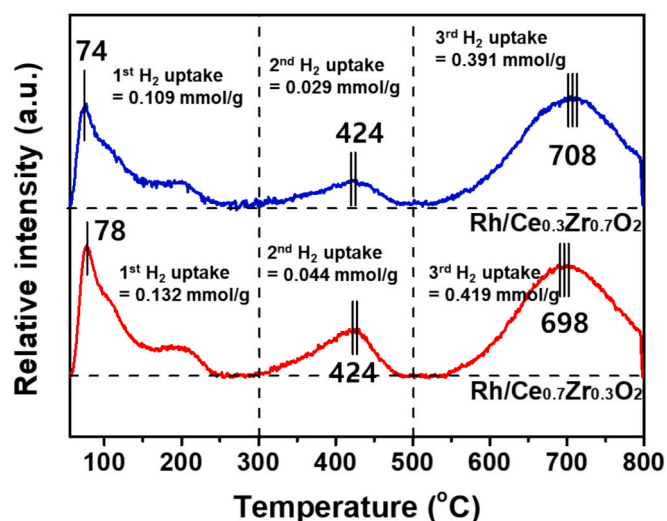


Fig. 6. H_2 temperature-programmed reduction (H_2 -TPR) of $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalysts after pretreatment in Ar for 1 h, followed by calcination in 10 % O_2/He at 400 °C for 1 h.

shell [26–28]. This confirms that Rh is primarily present in an oxidized state, dispersed form without the formation of metallic Rh clusters, as evidenced by the absence of Rh-Rh features typically observed near 2.7 Å in the metallic Rh reference [26–28]. In particular, the Rh-O peak intensity is very slightly higher for the cubic $\text{Rh}/\text{Ce}-\text{ZrO}_2$ catalyst, and the peak position is slightly shifted to higher compared to the tetragonal $\text{Rh}/\text{Ce}-\text{ZrO}_2$. This suggests a longer average Rh-O bond length in the cubic catalyst. The observed differences in both peak intensity and position indicate that the Ce/Zr ratio, which governs the crystal structure

of the support, plays a critical role in tuning the local geometry of Rh species. These structural changes, in combination with the XANES results, imply that Rh-support interactions are sensitive to the Ce- ZrO_2 structure and may influence catalytic performance in de- N_2O reactions. In addition to the first coordination shell, this FT-EXAFS results exhibit additional signals in the 2.0–3.0 Å range. These broad and weak features, observed for both cubic and tetragonal catalysts, are more reasonably assigned to Rh-O-Ce interactions rather than to the Rh-O-Rh second-shell contribution characteristic of the Rh_2O_3 reference [26–28]. In $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$, the Rh-O-Ce contribution in the 2.0–3.0 Å range was barely visible, suggesting that Rh atoms are weakly coordinated to Ce cations in the second shell. It is because oxygen vacancy rich interfaces in the cubic catalyst may cause structural disorder, further diminishing the Rh-O-Ce amplitude [26–28]. These characteristics indicate the presence of more reducible and weakly anchored Rh species, which can facilitate rapid redox cycling and oxygen spillover through the CeO_2 lattice, enhancing N_2O decomposition rate. In contrast, $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ exhibited a notable Rh-O-Ce feature, implying that Rh species are preferentially anchored to the limited Ce sites within the Zr-rich lattice [26–28]. It reflects a stronger metal-support bonding and greater structural stability but lower reducibility compared to the Ce-rich catalyst. Consequently, while $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ may exhibit higher oxidation resistance, its slower oxygen mobility and redox property could lead to reduced intrinsic N_2O decomposition rate. These interpretations are consistent with literature reports indicating that Ce-rich cubic $\text{Rh}/\text{Ce}-\text{ZrO}_2$ provides a more reducible environment and facilitate active Rh redox transitions, whereas Zr-rich tetragonal catalyst favor stabilized Rh-O-Ce linkage with stronger anchoring to the support [4–7]. (See Fig. 5).

H_2 -TPR experiments were performed to investigate the reduction properties of $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalysts. According to the literature, moreover, the N_2O decomposition reaction is closely related to the oxidation-reduction property of the catalyst so that we can

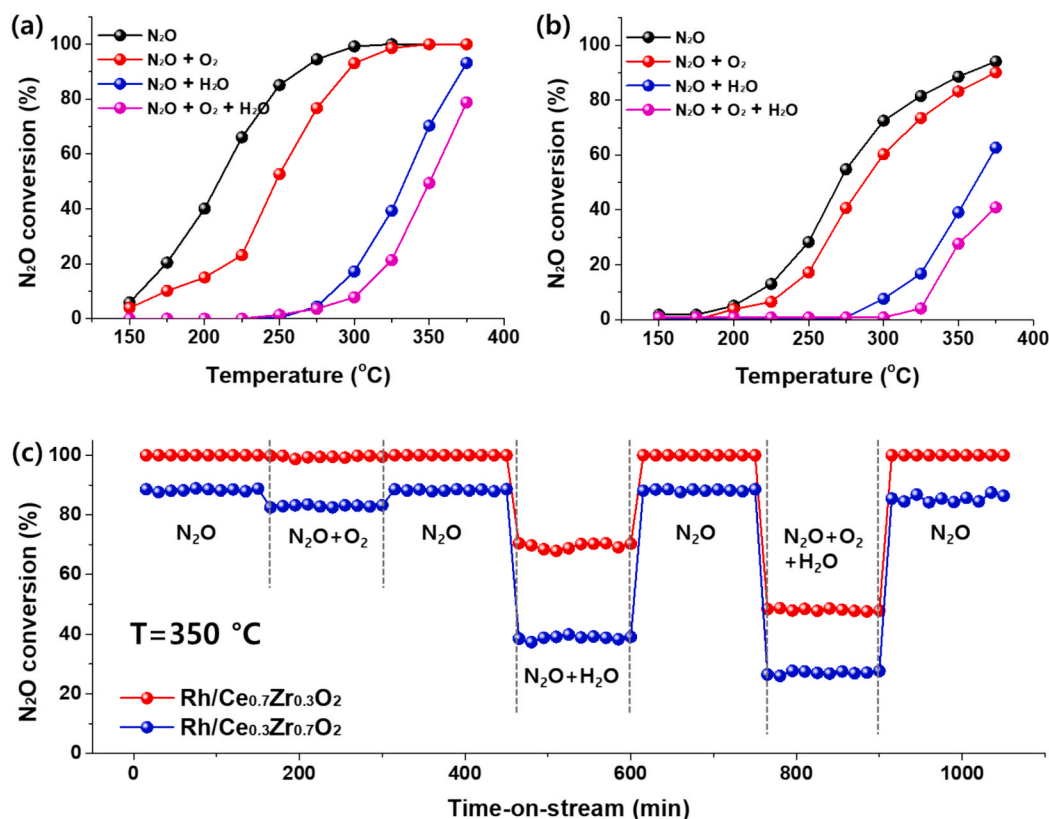


Fig. 7. N_2O conversion of $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ (a) and $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ (b) catalysts at $45,000 \text{ h}^{-1}$ of GHSV. Gas-switching experiments for the decomposition of N_2O (c). Conditions: 500 ppm N_2O , 500 ppm $\text{N}_2\text{O} + 3 \text{ } \text{O}_2$, 500 ppm $\text{N}_2\text{O} + 3 \text{ } \text{H}_2\text{O}$, and 500 ppm $\text{N}_2\text{O} + 3 \text{ } \text{O}_2 + 3 \text{ } \text{H}_2\text{O}$ in N_2 balance.

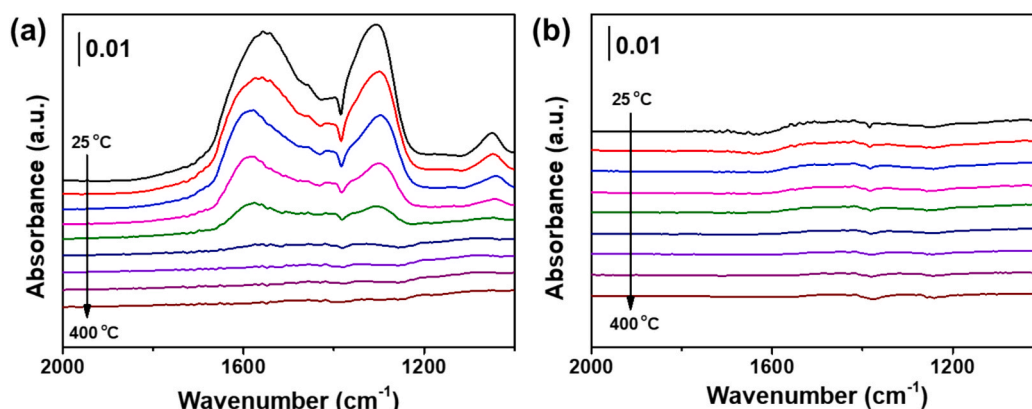


Fig. 8. Temperature programmed *in-situ* FT-IR spectra of Rh/Ce_{0.7}Zr_{0.3}O₂ (a) and Rh/Ce_{0.3}Zr_{0.7}O₂ (b) catalysts.

indirectly infer the catalytic performance. The H₂-TPR results are presented in Fig. 6. Basically, both catalysts show similar reduction behavior in the whole temperature range. The first peaks, appearing at approximately 75 °C, are assigned to the reduction of rhodium species interacting with the catalytic surface [7]. The second peaks, in the range of 300 °C to 500 °C, are attributed to the surface reduction of the Ce-ZrO₂ support, and the last peaks, between 500 °C and 800 °C, are ascribed to the bulk reduction of the Ce-ZrO₂ support [7]. Both catalysts show a similar reduction profile, but there is a difference in the amount of H₂ uptake at each temperature interval. The amount of H₂ reduction of the Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst (1st H₂ uptake = 0.132 mmol • g⁻¹, 2nd H₂ uptake = 0.044 mmol • g⁻¹, and 3rd H₂ uptake = 0.419 mmol • g⁻¹) is higher than that of the Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst (1st H₂ uptake = 0.109 mmol • g⁻¹, 2nd H₂ uptake = 0.029 mmol • g⁻¹, and 3rd H₂ uptake = 0.391 mmol • g⁻¹) at each temperature range. Assuming that all the rhodium oxide exists as Rh₂O₃, moreover, the theoretical H₂ consumption for 1 wt% rhodium oxide on the catalysts is 0.015 mmol • g⁻¹. However, the first H₂ uptake of Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts is 0.132 mmol • g⁻¹ and 0.109 mmol • g⁻¹, respectively. These values are much larger than the expected value for the reduction of Rh₂O₃ since peaks below 300 °C are attributed to the concurrent reduction of rhodium species and the Ce-ZrO₂ support [7]. This result is mainly because Rh promotes the reduction of the support, possibly through hydrogen spillover. Consequently, these variations are likely induced by the partial substitution of Zr⁴⁺ into CeO₂ or Ce⁴⁺ into ZrO₂, which modifies the metal-oxygen coordination environment, particularly the Ce-O-Ce and Ce-O-Zr linkages, leading to local structural and electronic changes [29].

The redox behavior of the Rh/Ce-ZrO₂ catalysts are governed by both chemical composition and crystallographic structure, and these two effects should be considered separately. The Ce/Zr ratio primarily determines the total amount of reducible oxygen because CeO₂ is the dominant redox-active component in the mixed oxide support. Consequently, catalysts with higher Ce content possess a larger population of potentially reducible oxygen species. However, the present results demonstrate that the reduction at low-temperature range are not solely dictated by Ce content. Despite the substantially higher Ce concentration in the cubic Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst, the increase in low-temperature H₂ consumption does not scale proportionally with Ce content, indicating that additional factors govern the reducibility under reaction-relevant conditions [30]. In this context, the crystallographic structure plays a crucial role in controlling the accessibility and mobility of lattice oxygen, as well as the efficiency of hydrogen spillover from Rh to the support. The cubic Rh/Ce-ZrO₂ catalyst facilitates faster oxygen migration and more dynamic Ce³⁺/Ce⁴⁺ redox cycling at the Rh-support interface, enabling a larger fraction of reducible oxygen to participate in low-temperature reduction [7,30]. In contrast, the tetragonal structure stabilizes oxygen species more strongly within the lattice, shifting a

significant portion of Ce reduction to higher temperatures. Therefore, while composition-driven effects govern the total reducible oxygen reservoir, structure-driven effects determine oxygen mobility, spillover efficiency, and the effective temperature window of reduction, which collectively influence the catalytic performance during N₂O decomposition.

3.2. Catalytic activity measurement

To evaluate the catalytic performance for N₂O decomposition, Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts, representing cubic and tetragonal structures respectively, were tested under both ideal and inhibition gas conditions. Fig. 7(a) and (b) presents the N₂O conversion profiles for both catalysts under these conditions. The Rh/Ce_{0.7}Zr_{0.3}O₂ catalyst exhibited an N₂O conversion of 85.1 % at 250 °C, which is approximately three times higher than the 28.3 % conversion achieved by the Rh/Ce_{0.3}Zr_{0.7}O₂ catalyst under ideal condition. Moreover, this cubic Rh/Ce-ZrO₂ catalyst maintained superior catalytic performance even in the presence of inhibition gases such as O₂ or H₂O. When a mixture of inhibition gas containing 3 % O₂ and 3 % H₂O was introduced into the feed simultaneously, the cubic catalyst retained a high N₂O conversion of 70 % at 350 °C, outperforming the tetragonal catalyst, which showed only 40.3 % conversion at the same temperature. Gas-switching experiments for N₂O decomposition were performed as a function of time-on-stream, as shown in the Fig. 7(c). The cubic Rh/Ce-ZrO₂ catalyst maintained nearly 100 % N₂O conversion throughout the stability test, whereas the tetragonal catalyst exhibited moderate but stable performance, maintaining approximately 70 % conversion. Furthermore, for both catalysts, the introduction of inhibition gas into the feed stream led to a noticeable decrease in catalytic activity. However, as clearly shown the catalytic activity decreases when the inhibition gas is added in the feed stream, but it is immediately recovered as soon as O₂ and/or H₂O were removed from the feed gas stream. It indicates that the deactivation is reversible and primarily governed by the reversible adsorption of inhibition gas species on the catalyst surface. These results clearly demonstrate that the cubic structure not only enhances initial activity but also contributes to the long-term stability in the presence of inhibition gas, likely due to the favorable electronic structure for de-N₂O reaction and high oxygen lability and reducibility between Rh and the support.

To further elucidate how N₂O interacts with catalysts possessing different crystal structures, *in-situ* FT-IR spectroscopy was conducted. This analysis observed the adsorption and decomposition behavior of N₂O on both cubic and tetragonal Rh/Ce-ZrO₂ catalysts. All spectra were recorded after exposing the samples to N₂O flow for 1 h at 25 °C, followed by purging under a He atmosphere to remove physisorbed species. Fig. 8 presents the temperature-dependent *in-situ* FT-IR spectra for Rh/Ce_{0.7}Zr_{0.3}O₂ and Rh/Ce_{0.3}Zr_{0.7}O₂ catalysts collected from 25 °C to

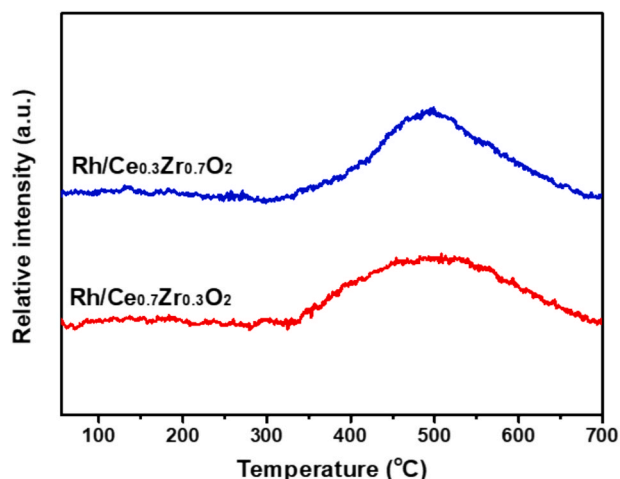


Fig. 9. O_2 temperature-programmed desorption (O_2 -TPD) of $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalysts after pretreatment in 10 % O_2/He at 50°C for 1 h, followed by calcination in He at 400°C for 1 h.

400°C . In the case of $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ (Fig. 8(a)), strong absorption bands were observed at 1552 , 1459 (shoulder), 1304 , 1049 , and 850 cm^{-1} after N_2O exposure at 25°C . According to literature, bands in the $1500\text{--}1400\text{ cm}^{-1}$ and $1570\text{--}1540\text{ cm}^{-1}$ regions can be attributed to monodentate nitrites and nitrates, respectively, while bands near 1350 cm^{-1} are typically assigned to nitro-type species [6,31]. The appearance of these bands implies that N_2O was oxidatively dissociated on the catalyst surface, forming various nitrogen-containing intermediates through interactions with $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst. By contrast, the $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalyst (Fig. 8(b)) exhibited only very weak and broad signals in the $1700\text{--}1200\text{ cm}^{-1}$ region, suggesting considerably lower N_2O uptake [6,31]. As the temperature increased from 25°C to 400°C , these characteristic band progressively diminished and disappeared for the $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst, indicating the thermal decomposition or desorption of surface-bound nitrogen species. However, no band change was observed for the tetragonal $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalyst over the same temperature range, suggesting limited reactivity with N_2O . The distinct IR bands observed on the cubic $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst are consistent with the high N_2O adsorption capacity confirmed by TGA analysis (Table 1) [7]. The *in-situ* FT-IR and TGA results demonstrate that the nature of the Ce-ZrO_2 support structure plays a critical role in governing N_2O adsorption and activation.

Previous *in-situ* IR studies have demonstrated that N_2O

decomposition over Rh/CeO_2 proceeds via dissociative adsorption of N_2O , accompanied by oxidation of interfacial Ce^{3+} species to Ce^{4+} , while the oxygen release from the catalyst surface is the rate determining step [30,32]. These studies further indicate that enhanced oxygen mobility and facile redox cycling of $\text{Ce}^{3+}/\text{Ce}^{4+}$ at the Rh -ceria interface are key factors governing sustained N_2O decomposition activity, particularly in the presence of O_2 and H_2O [30,32]. In the present work, O_2 -TPD experiments were performed to directly probe the mobility and release behavior of oxygen species from the $\text{Rh}/\text{Ce-ZrO}_2$ catalysts (Fig. 9). As shown in the O_2 -TPD results, the cubic $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst exhibits a higher oxygen desorption intensity and a broader desorption feature compared to the tetragonal $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalyst. This behavior indicates that oxygen species in the cubic $\text{Rh}/\text{Ce-ZrO}_2$ catalyst are more readily released, reflecting enhanced lattice oxygen mobility. In contrast, the tetragonal $\text{Rh}/\text{Ce-ZrO}_2$ catalyst shows lower oxygen desorption intensity, suggesting more strongly bound oxygen species and low oxygen mobility. The distinct O_2 -TPD behavior between the two catalysts suggests that the cubic $\text{Rh}/\text{Ce-ZrO}_2$ catalyst facilitates faster oxygen exchange and removal from the catalyst surface, which is essential for sustaining continuous redox cycling during N_2O decomposition (Fig. 10). When combined with the *in-situ* FT-IR observations, the O_2 -TPD results support a mechanism in which efficient removal of surface oxygen species preventing oxygen accumulation at the Rh -support interface, thereby maintaining active sites for continuous N_2O dissociation. The enhanced oxygen mobility evidenced by O_2 -TPD highlights the critical role of the Ce-ZrO_2 support in enabling dynamic redox behavior and superior catalytic performance.

4. Conclusion

This study presents a comprehensive comparison between cubic $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ and tetragonal $\text{Rh}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ catalysts for low-temperature N_2O decomposition, with a focus on the structure-activity relationship governed by the Ce/Zr ratio. The results reveal that the cubic $\text{Rh}/\text{Ce-ZrO}_2$ offers substantial advantages over the tetragonal $\text{Rh}/\text{Ce-ZrO}_2$ in terms of both catalytic performance and structural properties. Specifically, the cubic $\text{Rh}/\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst demonstrated superior N_2O conversion under both ideal and inhibition conditions, sustained high activity during time-on-stream stability tests, and rapid recovery from deactivation by reversible adsorption of inhibition gases. Characterization showed that this improvement is attributed to the property of cubic support structure ($\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$) to promote higher Rh dispersion, smaller Rh particle sizes, and greater oxygen mobility. Moreover, the cubic Ce-ZrO_2 facilitates higher Ce^{3+} concentration, relatively weak Rh -support interactions, and more favorable $\text{O}2p$ -metal

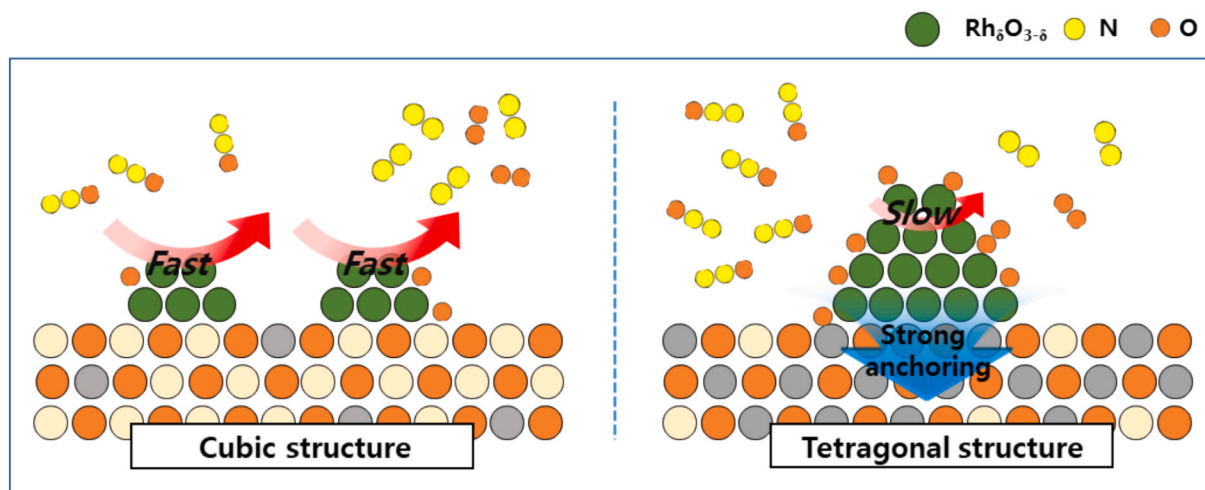


Fig. 10. A schematic illustration of N_2O decomposition over the cubic and tetragonal $\text{Rh}/\text{Ce-ZrO}_2$ catalysts.

hybridization near the surface. These electronic and structural features correlate with enhanced N_2O adsorption and activation, as evidenced by *in-situ* FT-IR and TGA results. In contrast, the low performance of the tetragonal Rh/Ce-ZrO₂ catalyst is primarily attributed to its low Rh dispersion with larger particle size and its low concentration of Ce³⁺ and surface oxygen vacancies, which together limit active site availability and hinder oxygen mobility essential for N_2O activation. These demonstrate that the crystal structure of Ce-ZrO₂ is a key structural parameter that governs the electronic environment and surface activity of active metal sites, determining the catalytic performance in N_2O decomposition.

CRediT authorship contribution statement

Jae-Rang Youn: Writing – original draft, Visualization, Data curation. **Honghe Ding:** Investigation, Data curation. **Yujian Xia:** Investigation, Formal analysis. **Jorge Moncada:** Investigation, Formal analysis, Data curation. **Roberto Colina-Ruiz:** Investigation, Formal analysis, Data curation. **Jinghua Guo:** Supervision, Project administration. **Min-Jae Kim:** Writing – original draft, Visualization, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2026.166042>.

Data availability

Data will be made available on request.

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