不同锆源对 $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ 整体式三效催化剂性能的影响陈山虎¹, 姚艳玲², 兰 丽¹, 曹 毅¹, 闫朝阳¹, 龚茂初¹, 陈耀强^{1,*}¹四川大学化学学院绿色化学与技术教育部重点实验室, 四川成都 610064²惠州学院化学工程系, 广东惠州 516007

摘要: 分别以 ZrOCO_3 , $\text{ZrO}(\text{NO}_3)_2$ 和 $\text{Zr}(\text{NO}_3)_4$ 为锆源采用双氧水氧化-共沉淀法合成了 $\text{Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ 储氧材料, 并用湿法浸渍法制备了 $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ 三效催化剂, 用 X 射线衍射、拉曼光谱、 N_2 吸附、X 射线光电子能谱、氢气程序升温还原和氧脉冲等技术对该催化剂进行了表征。结果表明, 以 ZrOCO_3 和 $\text{ZrO}(\text{NO}_3)_2$ 为锆源时所制催化剂上只能检测到单一的 CeO_2 - ZrO_2 立方相, 而以 $\text{Zr}(\text{NO}_3)_4$ 为锆源制备的催化剂经老化后却能检测到四方相; 另外, 在模拟汽车尾气组分和工作条件下考察了整体型 $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.9}$ 催化剂的三效活性。结果表明, 以 ZrOCO_3 为前驱体制备的整体式 $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.9}$ 催化剂对 C_3H_8 , CO 和 NO 具有最佳的催化活性。认为 ZrOCO_3 更有利于 Zr^{4+} 和 La^{3+} 进入 CeO_2 晶格形成均一固溶体, 从而提高催化剂的高温稳定性和氧化还原性能。

关键词: 储氧材料; 氧化共沉淀; 热稳定性; 氧化还原性能; 三效活性

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Effect of Zirconium Precursor on Performance of $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ Three-Way CatalystCHEN Shanhu¹, YAO Yanling², LAN Li¹, CAO Yi¹, YAN Chaoyang¹, GONG Maochu¹, CHEN Yaoqiang^{1,*}

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Abstract: Three types of $\text{Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ mixed oxides were prepared by H_2O_2 -assisted precipitation using ZrOCO_3 , $\text{ZrO}(\text{NO}_3)_2$, and $\text{Zr}(\text{NO}_3)_4$ as precursors. The $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ three-way catalysts were prepared by the wet impregnation and characterized by the X-ray diffraction (XRD), Raman spectroscopy, nitrogen adsorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and oxygen storage capacity. XRD and Raman spectroscopy results showed that the use of ZrOCO_3 or $\text{ZrO}(\text{NO}_3)_2$ gave a CeO_2 - ZrO_2 mixed oxide with a cubic phase of high thermal stability, while an extra t'' -phase was observed in the aged $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ catalyst prepared using $\text{Zr}(\text{NO}_3)_4$. The activities of the three catalysts were evaluated using simulated exhaust gas under working conditions. The $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ catalyst prepared using ZrOCO_3 as precursor gave the best activities for C_3H_8 , CO , and NO conversion. The use of ZrOCO_3 as precursor was better suited for the formation of Ce^{3+} and more favorable for the homogeneous insertion of Zr^{4+} and La^{3+} into the CeO_2 lattice, which resulted in better thermal stability and enhanced redox properties of the $\text{Pd/Ce}_{0.45}\text{Zr}_{0.45}\text{La}_{0.1}\text{O}_{1.95}$ catalyst.

Key words: oxygen storage material; oxidation-coprecipitation; thermal stability; redox property; three-way activity

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Automobile exhaust containing carbon monoxide, hydrocarbons, and nitrogen oxides are the major causes of air pollution, and three-way catalysts (TWCs) containing platinum group metals (Pt, Pd, and Rh) have received considerable attention for their purification. However, the pollutants can be together converted to harmless gases only if the air/fuel ratio is kept at around 14.6, which are lean fuel conditions [1]. Significant improvements in catalytic performance in a wider range of the air/fuel ratio have been achieved by incorporating CeO₂ into TWCs, which can act as an oxygen buffer for storing and releasing oxygen under lean and rich conditions, respectively [1–3].

However, pure CeO₂ will sinter at high temperatures, leading to a decrease in surface area and oxygen storage capacity (OSC). As a result, the catalyst performance will be severely degraded. In order to enhance thermal stability and retain the OSC of CeO₂, many binary materials, including CeO₂-ZrO₂, CeO₂-Y₂O₃, CeO₂-La₂O₃, and CeO₂-Al₂O₃, have been extensively investigated [2–9]. Among the tested materials, the CeO₂-ZrO₂ mixed oxide showed outstanding thermal stability and excellent redox properties, and its study has been an important direction of TWC development [1].

The thermal stability and redox properties of CeO₂-ZrO₂ can be enhanced by incorporating foreign ions such as Y³⁺ [2,3], La³⁺ [4], Al³⁺ [5], and Sr²⁺ [6] into its lattice. In particular, the adding of an appropriate amount of Y³⁺ and La³⁺ into a CeO₂-ZrO₂ mixed oxide promotes the homogeneous distribution of Ce and Zr on the atomic level, creates more defects, and enhances the redox ability. On the other hand, the properties of the materials are also determined by the preparation route. Many methods have been investigated to form CeO₂-ZrO₂-based materials with improved thermal stability and durability [2–18]. These include the precipitation method, sol-gel technique, hydrothermal route, high energy milling, and surfactant-assisted approaches. A requirement for an effective way to prepare the materials is that it should be suitable for large scale production application, thus the precipitation method is widely adopted because of its practicability.

The choice of starting materials also plays an important role in determining the properties of the product. A simple coprecipitation method using (NH₄)₂Ce(NO₃)₆ and ZrO(NO₃)₂ as cerium and zirconium precursors, respectively, was first employed by Hori et al. [7] to synthesize CeO₂-ZrO₂. The mixed oxide was successfully obtained by calcining the hydroxide at 500 °C. Rossingol et al. [8] found that a CeO₂-ZrO₂ solid solution could not be formed when Ce(NO₃)₃ was used as the cerium precursor, and two separated phases of cubic CeO₂ and tetragonal ZrO₂ were present in the final sample. Letichevsky et al. [9] have studied

the role of preparation conditions on the performance of the CeO₂-ZrO₂ samples and observed that the cerium precursor was the most important experimental parameter because it determined the existing phases and consequently the redox properties.

Since the 1980s, the H₂O₂-assisted precipitation method has been widely used by many researchers to prepare CeO₂-based materials [10–12]. It has been disclosed that H₂O₂ can oxidize Ce(III) to Ce(IV) in the presence of ammonia. The interaction of Ce³⁺, Zr⁴⁺, and H₂O₂ facilitates the formation of a CeO₂-ZrO₂ solid solution after thermal treatment [12]. However, no systematic research has been carried out to evaluate the influence of different zirconium precursors in the H₂O₂-assisted method. In this work, three different zirconium precursors were employed to synthesize a Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} support material to find the best zirconium precursor for Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} in the H₂O₂-assisted precipitation method. The textural, structural, and redox properties of the Pd/Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} catalysts and the catalytic activities for C₃H₈, CO, and NO conversion were investigated and correlated.

1 Experimental

1.1 Preparation of Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95}

All the supports in this work had the same nominal composition of Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95}. The Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} oxide was prepared by the H₂O₂-assisted precipitation method. First, ZrOCO₃ was dissolved by concentrated nitric acid. The molar ratio of ZrOCO₃:HNO₃ was 1:1. Then the required amounts of Ce(NO₃)₃ and La(NO₃)₃ were added under continuous stirring. Finally, a H₂O₂ solution of 30 wt% was introduced. The molar ratio of Ce:H₂O₂ was 1:1.5. After stirring for at least 1 h, an ammonia solution was added dropwise until the pH was 10. The precipitate was filtered, washed with distilled water till no pH change could be detected and then dried at 80 °C for 5 h. Finally, the sample was calcined at 600 °C for 3 h to get the fresh support, named CeZr1-F. The other two samples, using ZrO(NO₃)₂ or Zr(NO₃)₄ as precursors, were also prepared according to this procedure. The products were labeled CeZr2-F and CeZr3-F, respectively. For the heat treatment, the fresh samples were calcined at 1000 °C for 5 h to produce the aged oxides, which were denoted CeZr1-A, CeZr2-A, and CeZr3-A.

1.2 Catalyst preparation

The supported Pd catalysts with the fresh supports were prepared by the incipient impregnation method using

$\text{Pd}(\text{NO}_3)_2$ as Pd metal precursor. The Pd loading was 0.5 wt%. The samples obtained were dried at 120 °C for 12 h and calcined at 550 °C for 3 h. The powder was mixed with distilled water to prepare a slurry with 40 wt% solid content, which was coated onto cylindrical cordierite monoliths (Corning, USA, 400 cells/in²). The loading of washcoat was 140 g/L. The catalysts were dried at 120 °C for 12 h and calcined at 550 °C for 3 h to get the fresh samples. These samples were denoted as Pd/CeZr1-F, Pd/CeZr2-F, and Pd/CeZr3-F. Finally, the fresh samples were further aged at 1000 °C for 5 h in air to get aged catalysts, which were labeled as Pd/CeZr1-A, Pd/CeZr2-A, and Pd/CeZr3-A.

1.3 Catalytic activity measurement

The catalytic activity was measured in a fixed bed reactor. The simulated exhaust gas consisted of 8% NO, 6% C₃H₈, 0.86% CO, 12% CO₂, and 10% H₂O balanced with N₂. The space velocity was 34000 h⁻¹. C₃H₈, CO, and NO in the effluent were analyzed using a FGA-4100 analyzer (Foshan Analytical Instrument Co., LTD. China). The λ value, which was defined as the ratio between available oxygen and oxygen needed for the complete conversion of C₃H₈, CO, and NO, was expressed as $\lambda = (2[\text{O}_2] + [\text{NO}]) / (10[\text{C}_3\text{H}_8] + [\text{CO}])$. The amount of oxygen was controlled to give $\lambda = 1$ for the catalytic activity measurements. Prior to the measurement, the catalyst was treated under the reaction atmosphere at 550 °C for at least 1 h to ensure stable operation. The light-off performance was recorded by increasing the temperature stepwise from room temperature to 500 °C. At each point the temperature was maintained constant for at least 10 min.

1.4 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku DX-2500 diffractometer with Cu K α (40 kV,

200 mA). The data were collected from 10° to 90° with a step size of 0.03°. Raman spectroscopy was carried out on a LabRAM HR800 instrument with a diode laser source at a laser power of 150 mW. A frequency range of 200–2000 cm⁻¹ was recorded. X-ray photoelectron spectroscopy (XPS) experiments were carried out with a XSAM 800 spectrometer (KRATOS Corp.) with Mg K α radiation (13 kV, 20 mA). The binding energy (BE) of C 1s from carbon deposit was taken as reference and it was set to 284.6 eV to correct for charging effects.

The BET (Brunauer-Emmet-Teller) surface area and Barrett-Joyner-Halenda (BJH) pore size distribution were obtained on a Quantachrome SI instrument. Prior to the measurement, the samples were degassed under vacuum at 300 °C for 3 h. Oxygen storage capacity (OSC) experiments were performed by oxygen pulse injection technique at 200 °C over samples previously reduced in H₂ stream of 30 ml/min at 550 °C for 1 h. The oxygen consumption was monitored by a TCD detector. Temperature-programmed reduction (TPR) was conducted using a TCD detector with a U-tube containing 100 mg of sample. The samples were pretreated under flowing N₂ of 30 ml/min at 450 °C for 1 h and then cooled to room temperature. A reducing gas of 10% H₂/Ar of 30 ml/min was switched into the system and the temperature was raised from room temperature to 900 °C at a constant heating rate of 10 °C/min.

2 Results and discussion

2.1 XRD characterization

The XRD patterns of the fresh and aged catalysts are shown in Fig. 1. The main peaks at $2\theta = 29.1^\circ$ in the XRD patterns are the characteristic features of the cubic fluorite structure. No peak due to ZrO₂ or La₂O₃ was observed, which indicated that the Zr⁴⁺ and La³⁺ ions were incorporated into the CeO₂ lattice to form a solid solution [13]. It

Fig. 1. XRD patterns of fresh (a) and aged (b) catalysts.

has been reported that a CeO₂-ZrO₂ mixed oxide prepared by the coprecipitation method using Ce³⁺ as the cerium precursor shows structural heterogeneity, whereas a CeO₂-ZrO₂ solid solution is obtained when H₂O₂ is added into the mixed oxide reaction solution [9,14]. Therefore, our present result is in good agreement with previous works in the references.

The CeO₂-ZrO₂ phases are determined by the CeO₂ content. In the intermediate region, the nature of the CeO₂-ZrO₂ phase present is still under debate because of the presence of several metastable phases with tetragonal symmetry [15]. However, in this work, no tetragonal phase was observed although the molar ratio of Ce/Zr was 1:1, which indicated that the doping with La³⁺ enhanced the thermal stability of the cubic structure [9]. It was noted that the peak position of the sample prepared with ZrOCO₃ was shifted to a higher angle as compared with those prepared with ZrO(NO₃)₂ and Zr(NO₃)₄, thus the diffraction angles of the peaks followed the sequence of Pd/CeZr1-F > Pd/CeZr2-F > Pd/CeZr3-F. However, the particle sizes of the samples calculated from the XRD peak (Table 1) were in the order of Pd/CeZr1-F < Pd/CeZr2-F < Pd/CeZr3-F. We concluded that the use of different zirconium precursors led to differences on the crystal lattice level. The insertion of Zr⁴⁺ cations into CeO₂-ZrO₂ decreased its crystal parameter because the ionic radius of Zr⁴⁺ (0.084 nm) is smaller than that of Ce⁴⁺ (0.097 nm). The use of ZrOCO₃ facilitated the insertion of Zr⁴⁺ into the CeO₂-ZrO₂ lattice. This was further confirmed by XPS measurements presented in the following section.

Table 1 Lattice parameter and particle diameter of the different samples

Sample	D_{XRD}/nm	Crystallite parameter (nm)
Pd/CeZr1-F	4.7	0.5299
Pd/CeZr2-F	4.7	0.5329
Pd/CeZr3-F	4.8	0.5329
Pd/CeZr1-A	10.1	0.5284
Pd/CeZr2-A	10.8	0.5296
Pd/CeZr3-A	11.8	0.5326

As expected and shown in Fig. 1, after calcination at 1000 °C for 5 h, the oxides retained the cubic structure. However, the intensity of the XRD peaks became sharper, indicating the formation of larger crystallites caused by sintering. The average crystallite size of the aged samples was much larger than that of the fresh samples (Table 1). For the fresh samples, the particle size was almost constant, but after aging the particle sizes for Pd/CeZr1-A, Pd/CeZr2-A, and Pd/CeZr3-A increased to 10.1, 10.8, and 11.8 nm, respectively. The increase in crystallite size followed the sequence of Pd/CeZr3-A (151%) > Pd/CeZr2-A (130%) > Pd/CeZr1-A (115%), implying that the catalyst

prepared with ZrOCO₃ possessed the highest thermal stability.

It was also noted that the crystal parameters of Pd/CeZr1-F and Pd/CeZr2-F decreased significantly after the high temperature roasting. From the fact that the radius of Ce⁴⁺ is larger than Zr⁴⁺ and smaller than La³⁺, we deduced that enrichment of La³⁺ at the surface of CeO₂-ZrO₂ was the determining factor that caused the lattice shrinkage. On the other hand, the concentrations of oxygen vacancies and Ce³⁺ ions decreased with increasing crystallite size, inducing more Ce³⁺ (0.114 nm) to transform to Ce⁴⁺ (0.097 nm), which was the likely reason for the shrinkage of lattice parameter. In the case of Pd/CeZr3-A, the lattice parameter of the unit cell remained at almost the same value as Pd/CeZr3-F, which may be due to the balance between the agglomeration of Zr⁴⁺ and the extraction of La³⁺ from the bulk lattice. This was supported by the XPS results.

2.2 Raman spectrometry

The Raman spectra of the samples are shown in Fig. 2. The spectra were quite similar and were dominated by an intense absorption band at 470 cm⁻¹ with a weak band at 615 cm⁻¹ for the fresh samples (Fig. 2(a)). Only a band at 460 cm⁻¹ due to the fundamental F_{2g} mode vibration of the fluorite-type structure can be observed with pure CeO₂. However, some literature reports said this band actually occurs at 464 cm⁻¹ for CeO₂-based materials [16]. Therefore, the strong absorption line at 470 cm⁻¹ was assigned to the symmetric breathing mode of the oxygen atoms around the cerium ions. After aging at 1000 °C, the peak became intense (Fig. 2(b)), which was due to the better crystallization of the CeO₂-ZrO₂ solid solution calcined at the higher temperature. This was in agreement with the XRD results. In addition, as shown in Fig. 2, the intensity of this band in the different samples followed the sequence of Pd/CeZr3 > Pd/CeZr2 > Pd/CeZr1, indicating that the catalyst prepared with ZrOCO₃ had a relatively smaller crystallite size as compared with the others. This was another piece of evidence that demonstrated that the Pd/CeZr1-F catalyst had the highest thermal stability. The side band at 615 cm⁻¹ was attributed to oxygen vacancies induced by the presence of a defective structure in doped CeO₂ materials [17]. The intensity of the Raman spectra is affected by many factors, including particle size, morphology, and structure. With the increase of the calcination temperature, aggregation of the Zr-rich phase at the surface occurred, which was responsible for the shift of the band at 470 cm⁻¹ to lower values, as shown in Fig. 2(b). However, the vibration frequency of Pd/CeZr1-A was obviously higher than those of Pd/CeZr2-A and Pd/CeZr3-A, which implied that an improved insertion ability of ZrO₂ into the bulk of CeO₂ was

Fig. 2. Raman spectra of fresh (a) and aged (b) catalysts.

achieved in the case of using ZrOCO_3 . Furthermore, an extra band at 300 cm^{-1} was seen with Pd/CeZr3-A, which was attributed to the displacement of oxygen anions from their ideal fluorite positions, and indicated the segregation of the t'' phase in the lattice of the $\text{CeO}_2\text{-ZrO}_2$ solid solution. However, this metastable t'' phase cannot be effectively detected by the XRD technique due to the weak diffraction of oxygen atoms. The crystalline $\text{CeO}_2\text{-ZrO}_2$ solid solutions can be expected to be the monoclinic, tetragonal, or cubic phase, depending on the cerium content and calcination temperature, as reported in Ref. [15]. Accordingly, homogeneous $\text{CeO}_2\text{-ZrO}_2$ solid solutions can only be detected when the ZrO_2 molar percentage is $> 50\text{ mol}\%$. In the present work, no extra peak ascribable to tetragonal ZrO_2 was observed, suggesting that the insertion of trivalent La^{3+} cations into the $\text{CeO}_2\text{-ZrO}_2$ lattice improved the phase stability of the $\text{CeO}_2\text{-ZrO}_2$ solid solution. The intensity of the band at 615 cm^{-1} decreased in the order of Pd/CeZr1-A $>$ Pd/CeZr2-A $>$ Pd/CeZr3-A, which indicated that the defects in the sample prepared with ZrOCO_3 were better preserved during calcination.

2.3 XPS characterization

XPS measurements were carried out to investigate the surface elemental distribution and oxidation state of the cerium element of the catalyst. As illustrated in Fig. 3, there were eight peaks in the Ce 3d spectra corresponding to four pairs of spin-orbit doublets. The peaks labeled with “u” and “V” were the $3d_{3/2}$ and $3d_{5/2}$ spin-orbit components, respectively [13]. The peaks labeled (V_0, u_0), (V_2, u_2), and (V_3, u_3) were attributed to the states of Ce^{4+} , while the doublet (V_1, u_1) was due to Ce^{3+} . The XPS spectra disclosed the coexistence of Ce^{3+} and Ce^{4+} oxidation states in all the catalyst samples.

The proportion of Ce^{3+} was calculated from the ratio of

the areas of Ce^{3+} species to the sum of areas of all the cerium species (Table 2). The proportion of Ce^{3+} in the aged catalyst was lower than that in the fresh catalyst, which was caused by the oxidation of Ce^{3+} to Ce^{4+} during the calcination in air [16]. For both the fresh and aged catalysts, the concentration of Ce^{3+} ions decreased in the order of Pd/CeZr1 $>$ Pd/CeZr2 $>$ Pd/CeZr3.

In addition, by comparing the contents of the different elements, we concluded that the ratios of Zr and La on the

Fig. 3. Ce 3d XPS spectra for fresh (a) and aged (b) catalysts.

Table 2 Amounts of Ce, Zr, La, Pd, and O, and Ce³⁺ ratios determined from XPS spectra

Sample	Surface composition (%)					Zr/Ce	La/Ce	Ce ³⁺ in Ce (%)
	Ce	Zr	La	Pd	O			
Pd/CeZr1-F	9.49	8.83	2.00	1.41	78.27	0.93	0.21	22.72
Pd/CeZr2-F	6.93	10.35	1.75	1.26	79.70	1.52	0.25	20.40
Pd/CeZr3-F	7.08	11.47	2.21	1.18	78.05	1.62	0.31	20.12
Pd/CeZr1-A	9.03	9.40	2.13	1.22	78.22	1.04	0.24	18.91
Pd/CeZr2-A	5.31	8.82	1.58	0.98	83.30	1.66	0.30	18.66
Pd/CeZr3-A	4.40	9.07	1.55	0.56	84.41	2.06	0.35	18.56

surface of Pd/CeZr2-F and Pd/CeZr3-F were higher than those of Pd/CeZr1-F, indicating that the most homogeneous distribution of Ce, Zr, and La was in the Pd/CeZr1-F catalyst. This provided the interpretation for why the highest Ce³⁺ content was present in Pd/CeZr1-F, because the formation of a homogeneous CeO₂-ZrO₂ solid solution facilitated the reduction of Ce⁴⁺ to Ce³⁺ or the formation of oxygen vacancies [18]. Moreover, the surface Pd content of Pd/CeZr1-F was also higher than those of Pd/CeZr2-F and Pd/CeZr3-F, indicating that its Pd dispersion was higher than the others. On the other hand, after calcination at 1000 °C, an evident migration of Zr and La to the surface was observed, implying that a “shell-core” structure with a Zr-La-rich composition in the outer layer has been formed [18]. This new structure cannot be detected by XRD analysis because the crystallographic structure and orientation of the atomic planes are almost the same for the inner and outer regions of the crystallite. The Pd surface concentration for Pd/CeZr1-A was the largest among the catalysts, and its extent of decrease before and after aging was the lowest, suggesting that the use of ZrOCO₃ helped prevent Pd species from sintering and encapsulation.

2.4 Textural properties

The textural properties of the catalysts are listed in Table 3. All the fresh samples showed good textural properties with surface area and pore volume in excess of 100 m²/g and 0.25 cm³/g, respectively. The specific surface area and pore volume of the fresh samples were in the order of Pd/CeZr1-F > Pd/CeZr2-F > Pd/CeZr3-F, although the differences between them were not large. However, after cal-

Table 3 Textural properties of the samples

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{pore}}/(\text{cm}^3/\text{g})$	Average pore size (nm)
Pd/CeZr1-F	130	0.31	4.9
Pd/CeZr2-F	123	0.27	4.5
Pd/CeZr3-F	119	0.26	4.4
Pd/CeZr1-A	42	0.21	9.4
Pd/CeZr2-A	32	0.16	10.0
Pd/CeZr3-A	20	0.13	12.6

cination at 1000 °C, the differences between the different catalysts became remarkable. For example, the surface area and pore volume of Pd/CeZr1-A were 42 m²/g and 0.21 cm³/g, respectively, which were about twice those of Pd/CeZr3-A. The decrease in surface area and pore volume after calcination resulted from sintering at high temperature. The results showed that the textural properties were related to the zirconium precursor and indicated that the Zr precursor played an important role in the preparing of CeO₂-based materials. The formation of a homogenous CeO₂-ZrO₂ solution facilitates thermal stability during calcination. In this work, the use of different zirconium precursors led to different atomic distributions of Ce, Zr, and La, which were responsible for their differences in textural properties.

N₂ adsorption isotherms and pore size distributions of the fresh and aged samples are shown in Fig. 4. The isotherms of the Pd/CeZr1-F and Pd/CeZr2-F samples were Type IV with H₂ hysteresis, which is characteristic of mesoporous materials [19]. For Pd/CeZr3-F, the isotherm was Type II with H₃ hysteresis, suggesting the presence of ill-defined pseudo-mesopores [20]. The isotherm of Pd/CeZr3-A displayed the same characteristics as those of Pd/CeZr1-A and

Fig. 4. N₂ adsorption-desorption isotherms and pore size distributions of the fresh (a) and aged (b) catalysts.

Pd/CeZr2-A, implying that rearrangement of the pore structure of Pd/CeZr3-F occurred during aging. The pore size followed the sequence of Pd/CeZr1-F > Pd/CeZr2-F > Pd/CeZr3-F. After aging, the pore size distribution became wider because the sintering of mesoporous materials led to the elimination of small pores and formation of larger ones [18]. The growth rate of the pore size increased in the order of Pd/CeZr1-A < Pd/CeZr2-A < Pd/CeZr3-A, suggesting that the pore structure of Pd/CeZr1-F was thermally the most stable. From the viewpoint of pore structure, we attributed the excellent textural stability of Pd/CeZr1-F to its enlarged pore size. It has been reported that due to the need for long range migration, CeO₂-based materials with a larger pore size are difficult to sinter during thermal treatment.

2.5 H₂-TPR analysis

The reduction of the CeO₂-based materials used for TWCs is a crucial factor. Figure 5 displays the H₂-TPR profiles of the fresh and aged oxides. All the oxide samples showed a continuous reduction process consisting of an intense peak centered at 500 °C and an additional shoulder centered at 350 °C in the lower temperature region. The peak at 500 °C was associated with the reduction of CeO₂-ZrO₂. The shoulder at the lower temperature was ascribed to the reduction of surface adsorbed oxygen species or CeO₂-rich nanocrystallites dispersed at the interface of the mixed oxides crystallites [21]. The crystallite surface contains different O²⁻ ions with different coordination numbers. The surface of the oxide has defective structures such as steps, kinks, corners, and faces projecting O²⁻ ions, which increase with surface area. The reducibility of these O²⁻ species would be different, resulting in the shoulders in the profiles.

The reduction profile of CeO₂ usually shows two separate reduction steps, which were not observed in the present work. This was possibly because the high temperature re-

duction peak due to the bulk reduction of CeO₂ has disappeared. We deduced that the mobility of bulk oxygen species has been greatly improved by the high homogeneity of the CeO₂-ZrO₂ solid solution. The insertion of the trivalent cations, La³⁺, into the lattice of the CeO₂-ZrO₂ solid solution improved the oxygen storage capacity at low temperature by decreasing the onset of the reduction of the bulk of the solid solution as compared with the undoped case. Consequently, the removal of oxygen species occurs concurrently both at the surface and in the bulk of the mixed oxide. The reduction onset of CeZr1 was lower than those of CeZr2 and CeZr3, which might originate from its larger surface area because the surface reduction of CeO₂-ZrO₂ was expected to be correlated to its surface area [22]. Significant changes in reducibility occurred for the aged supports. As discussed above, the surface area decreased much after aging, and the mobility of the surface oxygen species was also much suppressed. On the other hand, the reduction of the bulk oxygen species mainly depended on the crystalline structure. The progressively increasing amounts of ZrO₂ and La₂O₃ inserted into the CeO₂ fluorite lattice enlarged the channel diameter for oxygen migration and increased structural defects, thus improving the reduction ability [23]. After aging, the migration of ZrO₂ and La₂O₃ from the bulk to the surface occurred, which degraded the mobility of lattice oxygen.

Figure 6 shows the H₂-TPR profiles of the catalysts before and after aging. All the fresh catalysts exhibited one intense peak (α) with a weak shoulder peak (β). According to the literature [18], the dominant α peak can be attributed to the reduction of highly dispersed PdO_x species, while β peak can be assigned to the reduction of stable PdO_x species. However, another possibility that involves stepwise reduction, i.e., the reduction of PdO to Pd₂O and the further reduction of Pd₂O to Pd cannot be excluded [24]. It should be pointed out that the consumption of hydrogen was much more than the nominal value. Considering the low loading

Fig. 5. H₂-TPR profiles of fresh (a) and aged (b) oxides.

Fig. 6. H₂-TPR profiles of fresh (a) and aged (b) catalysts.

of Pd, we speculated that the support also took part in the reduction process. This could occur because the presence of a noble metal could promote the removal of the interfacial oxygen species [25]. Two other weak peaks (δ and ϵ) in the range of 250–400 °C were also observed, which might be due to the reduction of surface/subsurface oxygen species. The reduction area of the samples decreased in the order of Pd/CeZr1-F > Pd/CeZr2-F > Pd/CeZr3-F, while the reduction onset was in the opposite order, indicating that the use of ZrOCO₃ was the best precursor with regard to the reduction of the catalyst.

In the case of the aged catalysts (Fig. 6(b)), the intensity of α' decreased significantly with respect to that of α , which was probably due to agglomeration of PdO_x particles caused by sintering or encapsulation [18]. Likewise, the β' peak might be due to surface/subsurface oxygen species from the support. Again the catalyst obtained using ZrOCO₃ had the best reducibility. Interestingly, an extra negative feature (γ) appeared in all the H₂-TPR profiles. This was induced by the decomposition of PdH_x, indicating the dissociation of hydrogen initiated by Pd at low temperature [25].

2.6 OSC measurements

The OSC values of the fresh and aged samples are shown in Fig. 7. For both the fresh and aged samples, the O₂ uptake followed the order of Pd/CeZr1 > Pd/CeZr2 > Pd/CeZr3. As shown by the XPS results, obvious segregation of Zr and La was observed on the surface of the samples except for Pd/CeZr1, indicating that Pd/CeZr1 has the most homogeneous structure, which would be responsible for its improved OSC. The OSC was also related to the surface area when this was lower than 50 m²/g, while the diffusion of oxygen from the bulk became the controlling step for high surface area CeO₂-ZrO₂ [27]. The surface areas of all the fresh samples were close to each other, thus, the OSC values were almost the same. After aging, the differences were

Fig. 7. OSC values of fresh and aged catalysts.

distinct, which contributed to the differences of the OSC values. Taking into account the surface area and surface available oxygen species, we deduced that the “less reducible” oxygen species were increased [13]. We also observed that Pd/CeZr1-A showed the highest OSC value among all the aged catalysts, which was attributed to its highest thermal stability.

2.7 Three-way catalytic activity

The conversions of C₃H₈, NO, and CO and light-off temperature (T_{50}) and complete conversion temperature (T_{90}) over the different catalysts are presented in Fig. 8 and Table 4. The Pd/CeZr1-F catalyst gave the best catalytic performance because its T_{50} and T_{90} for all the pollutants were the lowest among the tested fresh samples. Furthermore, the difference between T_{90} and T_{50} of Pd/CeZr1-F was the smallest, indicating that the catalyst could rapidly initiate and complete the reactions, which was very important to effectively purify pollutants produced in the cold start stage of the automobile. In addition, as compared with an earlier work [28], the Pd/CeZr1 catalyst even showed a better catalytic activity than the Pd/CZLA catalyst. Previous stud-

Fig. 8. Catalytic activities of fresh (a, c, and e) and aged (b, d, and f) catalysts.

Table 4 T_{50} and T_{90} for C_3H_8 , NO, and CO conversions over the different catalysts

Catalyst	$T_{50}/^{\circ}\text{C}$			$T_{90}/^{\circ}\text{C}$		
	C_3H_8	CO	NO	C_3H_8	CO	NO
Pd/CeZr1-F	295	94	103	318	119	125
Pd/CeZr2-F	303	102	112	332	133	138
Pd/CeZr3-F	319	113	117	347	139	144
Pd/CeZr1-A	299	145	154	344	160	173
Pd/CeZr2-A	320	155	162	359	179	179
Pd/CeZr3-A	345	161	172	390	180	207

ies [13,25] have disclosed that the reduction of surface PdO_x species, which were denoted as the α and β features in the present work, played an important role in CO and HC oxi-

dation. As for NO conversion, oxygen vacancies associated with the Ce^{3+} cations adjacent to the noble metal particles were supposed to be the active sites. Thus the abundant content of Ce^{3+} in Pd/CeZr1-F, as shown by Raman results, resulted in its superior efficiency for NO conversion. Based on the above analysis, the best redox property of the Pd/CeZr1-F catalyst was mainly responsible for its best catalytic performance. In the case of the aged catalysts, a large drop of the three-way activity was observed, which was attributed to the degraded structure and the sintering of the Pd component [13]. The sequence of catalytic activity of the aged catalysts was the same as that of the fresh ones. Apart from the reduction property, the structural and textural properties should also been taken into account due to

the high space velocity. A careful comparison of the OSC values and catalytic behavior of the aged catalysts indicated that the influence of OSC capacity could not be neglected. In the practical operation of a gasoline engine, the air/fuel ratio exhibits a slight oscillation around the stoichiometric point. Therefore, the OSC capacity is expected to be a crucial actor that determines the overall performance of the TWC.

3 Conclusions

The zirconium precursor played an important role in determining the catalytic performance of a Pd/Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} three-way catalyst. The use of ZrOCO₃ or ZrO(NO₃)₂ as Zr precursor gave Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} mixed oxides with the cubic phase, while an extra t'' phase was observed when Zr(NO₃)₄ was used as the Zr precursor. The Pd/Ce_{0.45}Zr_{0.45}La_{0.1}O_{1.95} catalyst prepared using ZrOCO₃ as Zr precursor exhibited the best textural, structural, and redox properties as well as the highest catalytic activity for the conversion of C₃H₈, CO, and NO. This was due to its having the most homogenous distribution of Ce, Zr, and La on the atomic level. In the oxidation-precipitation method, H₂O₂ gave some interaction between cerium and zirconium species, and the use of ZrOCO₃ resulted in zirconium species that best matched cerium species, which might be the reason for the formation of the homogeneous mixed oxide.

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