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Preparation of $Ce_xZr_{1-x}O_2$ ($x = 0.75$, 0.62) solid solution and its application in Pd-only three-way catalysts

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Abstract

Nanoparticles of $Ce_xZr_{1-x}O_2$ ($x = 0.75$, 0.62) were prepared by the oxidation-coprecipitation method using H_2O_2 as an oxidant, and characterized by N_2 adsorption, XRD and H_2-TPR. $Ce_xZr_{1-x}O_2$ prepared had single fluorite cubic structure, good thermal stability and reduction property. With the increasing of Ce/Zr ratio, the surface area of $Ce_xZr_{1-x}O_2$ increased, but thermal stability of $Ce_xZr_{1-x}O_2$ decreased. The surface area of $Ce_{0.62}Zr_{0.38}O_2$ was 41.2 m^2/g after calcination in air at 900 °C for 6 h. TPR results showed the formation of solid solution promoted the reduction of CeO_2, and the reduction properties of $Ce_xZr_{1-x}O_2$ were enhanced by the cycle of TPR-reoxidation. The Pd-only three-way catalysts (TWC) were prepared by the impregnation method, in which $Ce_{0.75}Zr_{0.25}O_2$ was used as the active washcoat and Pd loading was 0.7 g/L. In the test of Air/Fuel, the conversion of C_3H_8 was close to 100% and NO was completely converted at $\lambda < 1.025$. The high conversion of C_3H_8 was induced by the steam reform and dissociation adsorption reaction of C_3H_8. Pd-only catalyst using $Ce_{0.75}Zr_{0.25}O_2$ as active washcoat showed high light off activity, the reaction temperatures (T_{50}) of 50% conversion of CO, C_3H_8 and NO were 180, 200 and 205 °C, respectively. However, the conversions of C_3H_8 and NO showed oscillation with continuously increasing the reaction temperature. The presence of La_2O_3 in washcoat decreased the light off activity and suppressed the oscillation of C_3H_8 and NO conversion. After being aged at 900 °C for 4 h, the operation windows of catalysts shifted slightly to rich burn. The presence of La_2O_3 in active washcoat can enhance the thermal stability of catalyst significantly.

Keywords: $Ce_xZr_{1-x}O_2$; Oxidation-coprecipitation; Pd-only; Three-way catalyst

1. Introduction

Air pollution generated from automotive emission is a problem of general interest. Three-way catalyst (TWC) has been developed for the simultaneous elimination of three types of pollutant, i.e. carbon monoxide, hydrocarbons and nitrogen oxides, produced by non-perfect combustion and high temperatures in the combustion chamber. Further improvements in the preparation of TWC are needed in order to meet the more stringent future standards [1].

CeO_2 has been widely used in automotive emission control since 1980s because it can (1) store or release oxygen under lean or rich conditions; (2) promote the noble metal dispersion; (3) increase the thermal stability of Al_2O_3 support; (4) accelerate the water-gas shift and steam reforming reactions and (5) favor catalytic activity at the interfacial metal-support sites [1–4]. However, CeO_2 will deactivate significantly at high temperature due to the loss of surface area and oxygen storage capacity (OSC). In order to enhance the thermal stability and maintain the OSC of CeO_2, many CeO_2-based composites have been studied.

Pijolat et al. [5] have investigated the effects of different cation (i.e. Th^{4+}, Zr^{4+}, Si^{4+}, La^{3+}, Y^{3+}, Sc^{3+}, Al^{3+}, Ca^{2+} and Mg^{2+}) on the thermal stability of CeO_2. Among these foreign cations investigated, those with ionic radii smaller than that of Ce^{4+} can effectively stabilize CeO_2 against sintering. However, Kubsch et al. [6] have prepared the mixed oxides containing CeO_2 by coprecipitation method, and their results showed that the dopant whose radii are lager than that of Ce^{4+}, e.g. La, Nd, Y, can significantly stabilize CeO_2 due to the formation of solid solution. The thermal stability and redox properties of CeO_2–M_xO_y solid solution (M = Al, Si, Hf, Zr and so on) have also been investigated [7–12]. Among them, the CeO_2–ZrO_2 solid

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solution shows a good thermal stability and the best redox behavior, and achieve widespread utilization in three-way catalysts.

Nevertheless, not only the composition but the optimization of the manufacturing process is a key factor to obtain CeO_2–ZrO_2 solid solution with both high thermal stability and OSC. So far, various synthetic routes of CeO_2–ZrO_2 solid solutions were reported such as high-energy ball milling [13], reverse microemulsion [14], sol–gel techniques [15,16], coprecipitation [17,18], hydrothermal synthesis [19,20] and so on.

To obtain the CeO_2–ZrO_2 mixed oxide with better stability and redox property, many studies concentrated on the preparation of CeO_2–ZrO_2 solid solution with high stoichiometric and structural homogeneity. If CeO_2–ZrO_2 was prepared by coprecipitation using soluble Ce^{3+} and Zr^{4+} salt, the structural heterogeneity can be aroused [17]. It was possible to induced by the difference of precipitation speed of Ce^{3+} and Zr^{4+} ion, because of great difference of solubility product between $Ce(OH)_3$ (1.5×10^{-20}) and $Zr(OH)_4$ (2×10^{-48}). However, the solubility product of $Ce(OH)_4$ is 4×10^{-51} and close to that of $Zr(OH)_4$. Based on $Ce(OH)_3$ can be oxidized to $Ce(OH)_4$ by H_2O_2 immediately at the basic condition, a novel oxidation coprecipitation method was developed to prepare CeO_2–ZrO_2 solid solution in this paper.

In this paper, $Ce_xZr_{1-x}O_2$ ($x = 0.75$, 0.62) were prepared by oxidation coprecipitation method. The catalytic performances of Pd-only TWCs prepared using $Ce_{0.75}Zr_{0.25}O_2$ as active washcoat were studied.

2. Experimental

2.1. Preparation of sample

$Ce_{0.75}Zr_{0.25}O_2$ (CZ75) and $Ce_{0.62}Zr_{0.38}O_2$ (CZ62) solid solutions were prepared by the oxidation-coprecipitation method. Quantitative mixed aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ and $ZrO(NO_3)_2{\cdot}5H_2O$ was slowly added to the ammonia solution containing H_2O_2 under continuous stirring until pH 10. Then the mixture was moved into a Teflon-lined stainless steel autoclave, heated to 130–140 °C and kept at this temperature for 2 h. After hydrothermal treatment, yellow precipitate was filtered, washed with distilled water and ethanol several times, and subsequently dried at 110 °C in air overnight, then calcined at 500 or 900 °C for 6 h. As the reference, $Ce_{0.62}Zr_{0.38}O_2$ (CZ62-cc) was prepared by the same procedure without adding H_2O_2.

The cordierite monoliths (Corning, 62 cell/cm^2) with the diameter of 22 mm and length of 21 mm after cutting were cleaned by calcination at 900 °C in air for 2 h. The slurry of washcoating consisted of 25 g CZ75 prepared, suitable amount of boehmite and/or 10 g $La(NO_3)_3$ in 100 mL of water, and pH of slurry was adjusted to 5 under stirring by adding a nitric acid aqueous solution. The washcoating was carried out by immersing the cordierite monolith in the slurry for 5 min. In order to be sure the slurry went into the channels of monolith, the monolith was outgassed at room temperature for 15 min, then the immersion was performed under vacuum. Afterward, the washcoated monolith was blown with air to remove the excess of slurry, dried at 110 °C overnight and calcined at 650 °C for 3 h.

The Pd-only three-way catalysts were prepared by the impregnation of washcoated cordierite monolith with palladium acetate dichloromethane solution. Pd loading was 0.7 g/L. The washcoat was comprised of Al_2O_3, La_2O_3 and CZ75 in the PdCZL catalyst. The PdCZ catalyst was prepared by the same procedure as PdCZL except for the addition of La_2O_3. The ''fresh catalysts'' were dried by an infrared lamp and calcined in air at 400 °C for 3 h. The fresh catalysts were calnined at 900 °C for 4 h to get the aged catalysts.

2.2. Characterization of sample

The BET surface area of $Ce_xZr_{1-x}O_2$ was measured by nitrogen adsorption at 78.3 K using a ST-03A Instrument of surface area and pore size distribution (Beijing Analytic Instrument Plant). The X-ray diffraction (XRD) were recorded on a Rigaku D/MAX/2550/PC diffractometer using Cu Kα radiation ($\lambda = 1.54056$ Å).

Temperature programmed reduction (TPR) studies were carried out in a conventional system equipped with a thermal conductivity detector (TCD). Sample was firstly treated at 500 °C for 1 h in air, and then cooled to room temperature in 20 cm^3/min N_2 flow. TPR was performed by heating the sample in the flow of 8%H_2 in N_2 (25 cm^3/min) at a heating rate of 10 °C/min.

2.3. Catalytic activity test

The activity of Pd-only three-way catalyst was tested in the fixed-bed reactor with the simulated exhaust gas containing CO (3%), C_3H_8 (5000 ppm), NO (5000 ppm), CO_2 (10%), O_2 and N_2 (balance). The space velocity was 30,000 h^{-1}. The concentration of O_2 was adjusted in the tests of light off and Air/Fuel ratio. λ is defined as $\lambda = 2V_{O_2} + V_{NO}/10V_{C_3H_8} + V_{CO}$, $\lambda = 1$ is at stoichiometry. In the light off experiment, temperature was programmed from 30 to 350 °C at a rate of 4 °C/min at $\lambda = 0.99$. The Air/Fuel ratio experiment were carried out at the temperature of 500 °C. The contents of CO, NO and total HC were recorded by a FGA-4100 Automotive Emission Analyzer (Foshan, China).

3. Results and discussion

3.1. XRD and BET

The XRD patterns of $Ce_xZr_{1-x}O_2$ calcined at different temperature are shown in Fig. 1. For $Ce_xZr_{1-x}O_2$ calcined at 500 °C, all samples showed single fluorite cubic structure [14], and the characteristic diffraction peaks slightly shifted to higher 2θ degree with the increase of ZrO_2 content. It reveals the decrease of lattice parameters of $Ce_xZr_{1-x}O_2$ induced by the substitution of small Zr^{4+} ion ($r = 0.084$ nm) for Ce^{4+} ($r = 0.097$ nm) in the preparation process. After calcination at 900 °C for 6 h, CZ62 and CZ75 showed stronger diffraction peaks, and the diffraction peaks of single oxide were not observed. For CZ62-cc calcined at 900 °C for 6h, the phase

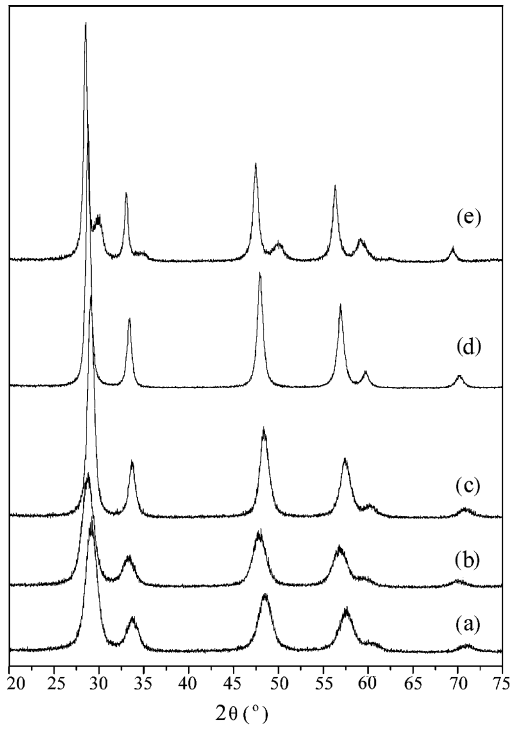

Fig. 1. XRD patterns of CZ62 (a and c), CZ75 (b and d) and CZ62-cc (e). (a and b: calcinated at 500 °C for 6 h; c, d and e: calcined at 900 °C for 6 h).

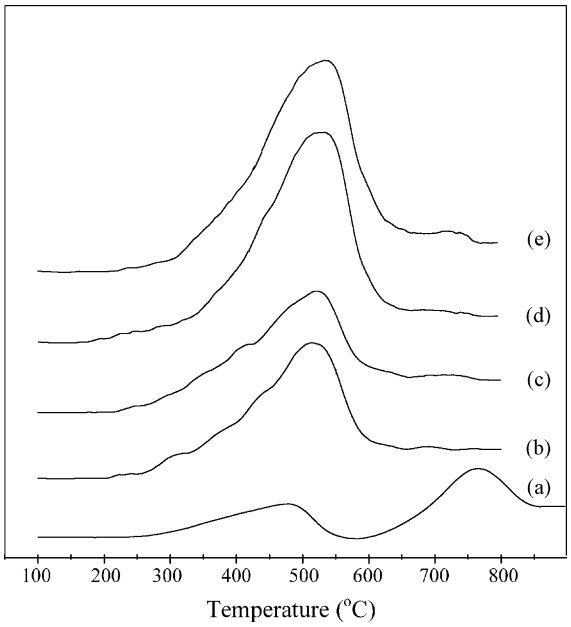

Fig. 2. TPR profiles of pure CeO_2 (a), CZ75 (b and d) and CZ 62 (c and e). (b and c was first run; d and e was third run).

separation occured. The characteristic peaks of ZrO_2 were observed at about 30, 35, 50 and 60°. It indicates that $Ce_xZr_{1-x}O_2$ prepared by oxidation-coprecipitation method has the good structure homogeneity and high thermal stability.

The average particle sizes of $Ce_xZr_{1-x}O_2$ estimated by line-broadening method [21] are summarized in Table 1. The results showed that the particles grew up significantly after calcination at 900 °C. The growth degree of particle size $((D_{900°C}–D_{500°C})/D_{500°C})$ of CZ62 was 70% and smaller than that of CZ75 (78%), which indicated that the increase of ZrO_2 content was available to enhance the thermal stability of $Ce_xZr_{1-x}O_2$ solid solution.

The results of BET surface area showed that composition of $Ce_xZr_{1-x}O_2$ can influence the surface area of sample significantly (Table 1). For the sample calcined at 500 °C, CZ75 showed higher surface area than CZ62. However, CZ62 had the higher thermal stability than CZ75, and its surface area was 41.2 m^2/g after calcination at 900 °C for 6 h.

3.2. H_2-TPR

The H_2-TPR test is used to characterize the redox properties of $Ce_xZr_{1-x}O_2$ solid solution. The TPR profiles of $Ce_xZr_{1-x}O_2$ and pure CeO_2 (prepared by the same procedure) are shown in Fig. 2. Two peaks at about 500 and 800 °C were found in the TPR profile of CeO_2, which were associated with the reduction at the surface and in the bulk of CeO_2 [2]. CZ75 showed the similar reduction profile with CZ62, a broad reduction peak in the temperature range 250–650 °C can be observed. The surface and bulk reduction was not distinguished clearly on CZ75 and CZ62, which indicated that the formation of $Ce_xZr_{1-x}O_2$ solid solution enhanced the bulk reduction of CeO_2. The total H_2 uptake calculated between 200 and 800 °C showed that the reduction properties of $Ce_xZr_{1-x}O_2$ solid solution increased with the increase of ZrO_2 content.

In the TPR-reoxidation cycle, the reduction peak of $Ce_xZr_{1-x}O_2$ became more remarkable, and shifted slightly to higher temperature (Fig. 2d and e). It was noticed that both CZ75 and CZ62 showed lower total H_2 uptake after calcination at 900 °C for 6 h in our experiments. It indicates that the treatment condition can influence the reduction properties of $Ce_xZr_{1-x}O_2$ dramatically, which is in agreement with the results of Vidal et al. [22].

Fornasiero et al. [23] have observed the reduction peaks of $Ce_{0.5}Zr_{0.5}O_2$ at lower temperature in the repetitive reduction/oxidation cycle, and the amount of H_2 consumption increased slightly after the reduction/oxidation cycle. Vidal et al. [22] have found that the oxygen storage capacity of $Ce_{0.68}Zr_{0.32}O_2$

Table 1
BET surface areas and average particle sizes of CeO_2–ZrO_2 solid solution

Sample	BET surface area (m^2/g)		Particle size (nm)		
	500 °C/6 h[a]	900 °C/6 h	500 °C/6 h	900 °C/6 h	$(D_{900°C}–D_{500°C})/D_{500°C}$
CZ75	133.9	22.6	5.4	9.6	0.78
CZ62	106.7	41.2	5.3	9.0	0.70

[a] Calcination condition.

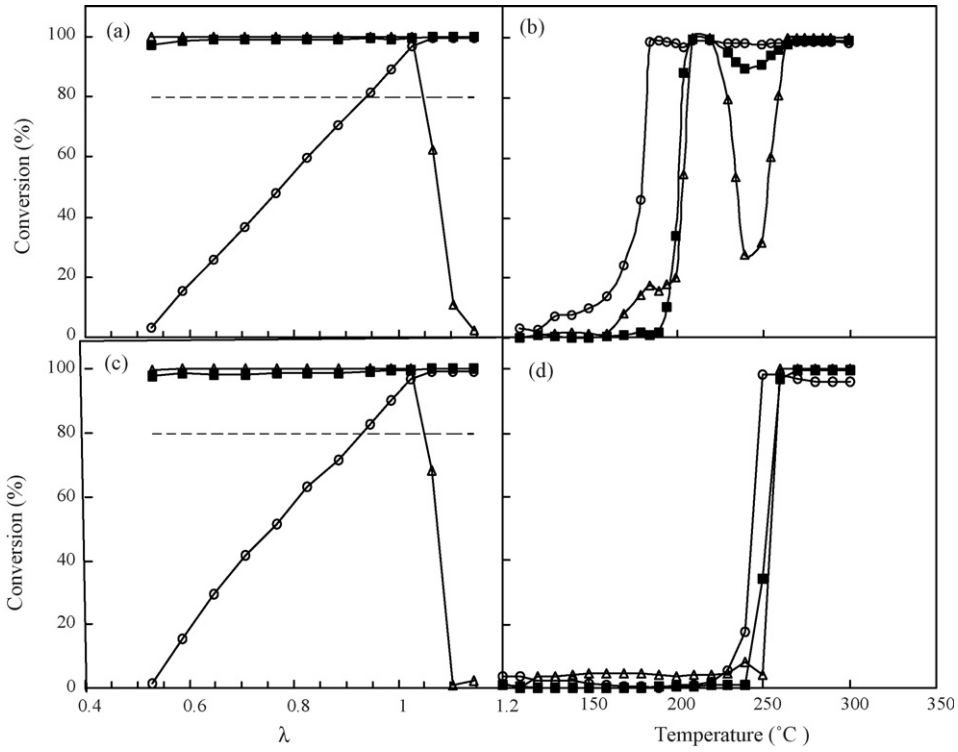

Fig. 3. Conversion curves of C_3H_8 (■), CO (○) and NO (△) as a function of Air/Fuel ratio (λ) and temperature over fresh PdCZ (a and b) and PdCZL (c and d).

can be improved after being aged in H_2, and OSC increases significantly with increasing the treatment temperature. Nagai et al. [24] have reported that the surface area of $Ce_{0.5}Zr_{0.5}O_2$ decreases from 89 to 1 m^2/g after severe reduction treatment, however its OSC increases from 9.9 to 1500 μmol-O/m^2.

Many studies show that the composition of CeO_2–ZrO_2, preparation method, pretreatment condition, structural homogeneity and textural property can influence the OSC and thermal stability of solid solution. Among them, the homogeneous degree of structure plays an important role in enhancing the redox properties of $Ce_xZr_{1-x}O_2$. The change of phase structure of $Ce_xZr_{1-x}O_2$ can occur inevitably due to the transformation of Ce^{4+} to Ce^{3+} in the reduction process [25]. The rearrangements of Ce and/or Zr ions in the reoxidation process possibly induce the enhancement of homogeneity of $Ce_xZr_{1-x}O_2$ solid solution, which is available for the improvement of its OSC.

3.3. Catalytic activity

The results of Air/Fuel (λ) and light off tests over fresh catalysts are shown in Fig. 3. In the Air/Fuel test (Fig. 3a and c), the conversions of C_3H_8 were close to 100% on both catalysts, and NO can be completely converted at $\lambda < 1.025$. NO conversion decreased sharply with continuously increasing O_2 content, and no obvious conversion of NO can be detected at $\lambda = 1.145$. It was interesting that CO conversion increased linearly with increasing O_2 content, and oxygen seemed to oxidize CO only.

The relationship of CO conversion with λ can be derived based on the assumption that oxygen was used to oxidize CO only in the λ range of 0.527–1.025, the results are listed in Table 2. The slight difference of slope was aroused by different CO content at $\lambda = 0.527$ over PdCZ and PdCZL. The linear relationship of CO conversion with λ was also derived from the experimental data between $\lambda = 0.527$ and 1.025, and linear correlation coefficient (R^2) was very close to 1 (Table 2).

The slop derived from experiment was about 66–69% of the calculated value. The great difference of slope indicated that there were other oxidation reactions in addition to the CO oxidation. In general, C_3H_8 can be transferred via the following routes:

$$\text{Combustion}: \quad C_3H_8 + O_2 \rightarrow CO_2 + H_2O \tag{1}$$

$$\text{Partial oxidation}: \quad C_3H_8 + O_2 \rightarrow CO + H_2O \tag{2}$$

Oxidative dehydrogenation :

$$C_3H_8 + O_2 \rightarrow C_3H_6 + CO_x + H_2O$$

Table 2
Relationship of CO conversion with λ

Catalyst	Experimental		Calculated equation
	Equation	R	
PdCZ	%CO = 187.14λ − 95.11	0.9999	%CO = 282.94λ − 148.73
PdCZL	%CO = 187.63λ − 93.74	0.9962	%CO = 271.11λ − 142.44

$$\text{Oxidation}: \quad C_3H_8 + CO_2 \rightarrow C_3H_6 + C_1 + C_2 + CO + H_2O \tag{4}$$

$$\text{Oxidation}: \quad C_3H_8 + NO_x \rightarrow CO_x + N_2 + H_2O \tag{5}$$

$$\text{Dehydrogenation}: \quad C_3H_8 \rightarrow C_3H_6 + C_1 + C_2 + H_2 \tag{6}$$

$$\text{Dissociative adsorption}: \quad C_3H_8 \rightarrow HC^* + H_2 \tag{7}$$

$$\text{Steam Reform}: \quad C_3H_8 + H_2O \rightarrow CO + H_2 \tag{8}$$

Reaction (3), (4) and (6) can be excluded based on the fact that no obvious hydrocarbsons were observed in λ range of 0.527–1.025. It was noted that CO content of outlet was higher than that of inlet when λ = 0.527 in the experiments, which indicated that C_3H_8 can be consumed almost completely, and CO released at the same time.

For the C_3H_8 oxidation in substoichiometry of oxygen ($[O_2]/5[C_3H_8] = 0.4$), the complete conversion of C_3H_8 was obtained by a contribution of secondary steam reforming reaction, corresponding to the reaction of C_3H_8 with water produced by oxidation, when oxygen was consumed totally [26]. But the C_3H_8 oxidation/partial oxidation, reaction (1), (2) and (5), were the competitive reactions against CO oxidation, and the latter was more easily occurred. The existence of CO was unavailable for the further steam reform reaction (reaction (8)). Many studies indicated that the hydrocarbon can be chemisorbed on the metallic surface at mild temperature, and the dissociation reaction can occur at higher temperature [27–29]. So the reaction (7) was also possible in the substoichiometric oxygen condition.

Based on the evaluation of reaction condition, the reaction (1), (2), (5), (7) and (8) were possible when $\lambda < 1$. Among them, the reaction (7) and (8) maybe played the major role in maintaining the high conversion of C_3H_8. Part of O_2 was used to oxidize CO, and the other was used to oxidize H_2 and/or HC^* produced in the reaction (7) and (8). Furthermore, NO can be reduced by H_2 via the following reaction: $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$. In fact, the formation of NH_3 was observed at $\lambda < 1$ in our experiments.

In the light off test (Fig. 3b and d), PdCZ showed higher activity than PdCZL. The temperatures (T_{50}) of 50% conversion of CO, C_3H_8 and NO were 180, 200 and 205 °C over PdCZ, respectively (Fig. 3b). However, the oscillating conversions of C_3H_8 and NO were observed with continuously increasing the reaction temperature.

Deng and Nevell [30] observed the oscillation process of methane combustion over supported Pd catalyst. The chemical state of Pd can influence the oxidation of alkane greatly. The catalyst having optimum ratio of metallic palladium to palladium oxide showed the highest catalytic activity in the propane combustion [26,31].

The TPR profiles of different catalysts are shown in Fig. 4. Three main reduction peaks can be observed in the temperature range of 50–500 °C. Among them, γ peak can be attributed to the reduction of CeO_2–ZrO_2 [1,2]. Comparing with the results in Fig. 2, the reduction peak of CeO_2–ZrO_2 shifted to lower temperature, which was attributed to the presence of Pd promoting the reduction of CeO_2 via spilling of hydrogen

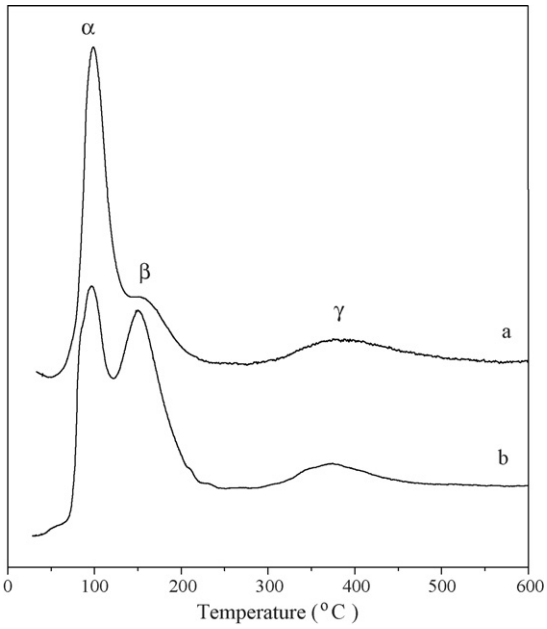

Fig. 4. TPR profiles of PdCZ (a) and PdCZL (b).

species over the support [1,2]. PdO can be reduced to metallic Pd at the temperature lower than 200 °C [32–35]. Barrera et al. [33,34] reported that two reduction peaks of Pd/La_2O_3–Al_2O_3 were observed at 100 and 150 °C, and suggested that crystalline PdO can be reduced in two stages: $2PdO + H_2 \rightarrow Pd_2O + H_2O$ and $Pd_2O + H_2 \rightarrow Pd + H_2O$. The similar results were obtained on Pd/CeO_2 and La doped Pd/CeO_2 [35]. The TPR profile of PdCZL showed two comparable reduction peaks (α and β) at 100 and 135 °C, which was in agreement with the results in references [33–35] and assigned to the two stages reduction of PdO. In the TPR profile of PdCZ, two reduction peaks were also observed at the temperature lower than 200 °C, but the area of α peak was much larger than that of β peak. This suggested that the most of PdO was reduced in only one step [34]. It indicated that the presence of La_2O_3 on PdCZL hindered the reduction of PdO and helped PdO to maintain a more cationic state. Subramanian et al. [32] reported that the increase of ability of oxygen transfer on ceria–lanthana interface can hinder the reduction of PdO.

For the PdCZ catalyst, PdO was reduced to Pd^0 under reducing condition (λ = 0.99), which resulting in the decrease of the catalytic activity for C_3H_8 oxidation. Therefore, oxygen cannot be consumed completely, and the existence of residual oxygen led to the significant decrease of NO conversion. With increasing the reaction temperature, Pd^0 was reoxidized to PdO_x ($0 < x \leq 1$) by residual oxygen in the reaction gas and the activity of catalyst recovered. Furthermore, higher reaction temperature can accelerate the catalytic oxidation of C_3H_8 despite of the chemical state of Pd.

The presence of La_2O_3 affected the interaction between PdO and CeO_2–ZrO_2, and decreased the catalytic activity of PdCZL. However, the oscillating conversions of C_3H_8 and NO were not observed over PdCZL (Fig. 3d). It was supposed that the presence of La_2O_3 inhibited the reduction of PdO and kept the catalyst PdCZL in an active state for C_3H_8 oxidation. At the same time, another possibility can also suppress the oscillation

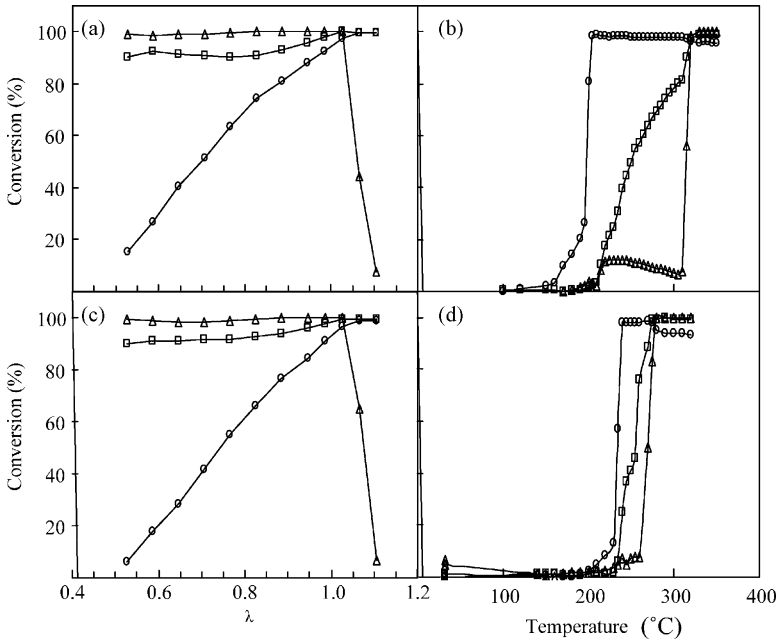

Fig. 5. Conversion curves of C_3H_8 (□), CO (○) and NO (■) as a function of Air/Fuel ratio (λ) and temperature over aged PdCZ (a and b) and PdCZL (c and d).

of conversions. It was that PdCZL did not show activity in the temperature range of oscillation taking place on PdCZ due to its lower activity. Certainly, the nature of oscillation of conversion needs to be investigated further.

Fig. 5 shows the catalytic performance of the catalysts aged. Both catalysts had the similar Air/Fuel ratio properties. Comparing with the results in Fig. 3, the operating window shifted to rich burn. After being aged, the light off activity of PdCZ decreased significantly, T_{50} of CO, C_3H_8 and NO were 195, 250 and 315 °C, respectively. As a good promoter, La_2O_3 was often used to improve the thermal stability of Al_2O_3, CeO_2–ZrO_2 and supported Pd catalyst [14,36,37]. The presence of La_2O_3 in PdCZL enhanced the thermal stability of catalyst, T_{50} of CO, C_3H_8 and NO was 235, 260 and 270 °C, respectively.

4. Conclusions

Nanoparticles of $Ce_xZr_{1-x}O_2$ ($x = 0.75, 0.62$) can be prepared by the oxidation-coprecipitation method using H_2O_2 as oxidant. The surface area of $Ce_xZr_{1-x}O_2$ increased with increasing of Ce/Zr ratio, but the thermal stability of $Ce_xZr_{1-x}O_2$ decreased. The BET surface area of $Ce_{0.62}Zr_{0.38}O_2$ was 41.2 m^2/g after calcination in air at 900 °C for 6 h. After the TPR-reoxidation cycle, the reduction property of $Ce_xZr_{1-x}O_2$ was improved.

In the Air/Fuel test, the conversions of C_3H_8 was close to 100% and NO can be completely converted at $\lambda < 1.025$. The high conversion of C_3H_8 may profit from the steam reform and dissociation adsorption reaction of C_3H_8. NO can be reduced by H_2 to produce NH_3 when $\lambda < 1$.

Fresh Pd-only catalyst using $Ce_{0.75}Zr_{0.25}O_2$ as active washcoat had a high light off activity, the temperatures of 50% conversion of CO, C_3H_8 and NO were 180, 200 and 205 °C, respectively. However, the conversions of C_3H_8 and NO showed oscillation with continuously increasing the reaction temperature. The presence of La_2O_3 in washcoat deceased the light off activity, and eliminated the oscillation phenomena of C_3H_8 and NO conversion.

After being aged at 900 °C for 4 h, the operation windows of catalysts shifted to rich burn. The presence of La_2O_3 in active washcoat enhanced the thermal stability of catalyst significantly, the temperatures of 50% conversion of CO, C_3H_8 and NO were 235, 260 and 270 °C, respectively.

Acknowledgements

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