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Article

The effect of Pd precursor on Pd/Ce_{0.67}Zr_{0.33}O₂ catalysts for automotive emission control

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ABSTRACT

A Pd/CZ(NO) catalyst prepared with Pd(NO₃)₂ as the metal precursor exhibited the best catalytic performance for HC and CO elimination because of a higher oxygen storage capacity, abundant small Pd_n clusters and a strong Pd-support interaction that facilitated electron transfer from PdO_x particles to the CZ support. A Pd/CZ(NH) catalyst prepared with Pd(NH₃)₄(NO₃)₂ as the metal precursor exhibited good performance for NO and NO₂ elimination due to a higher Pd dispersion, abundant bigger Pd_n clusters and oxidized/metallic Pd coexistence. A Pd/CZ(Cl) catalyst prepared with H₂PdCl₄ as the metal precursor exhibited low catalytic activity due to a low Pd dispersion, weak Pd-support interaction, and the trace amount of CeOCl which inhibited oxygen vacancy creation. However, it showed good thermal stability, and benefited when an aging treatment removed the residual chlorine species and also promoted the interaction between PdO_x and the support.

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1. Introduction

Three-way catalysts (TWCs) are extensively used to diminish pollutant emissions from gasoline automobiles. The classical components of these systems are Rh, Pt, and Pd as active metals and Ce-Zr mixed oxide as promoter. The use of Pd as a single active metal in TWCs has recently gained increasing attention due to the high cost and scarcity of Rh and its high activity for oxidation reactions [1–5]. Since the simultaneous conversions of HC, CO, and NO_x are strongly affected by the oxygen partial pressure, Ce-Zr mixed oxides with an inherent property to release or adsorb oxygen have been widely used. Ceria is recognized as the chief oxygen storage material because of its facile redox cycling through the Ce³⁺/Ce⁴⁺ cycle. It also has the ability to increase the thermal and structural stability of the catalyst carrier [6]. The introduction of zirconia into the ceria lattice can significantly increase the oxygen va-

cancies in the fluorite lattice by charge compensation, facilitate oxygen diffusion or transport and enhance the thermal stability of the solid solution [7]. Better results are obtained with Ce_xZr_{1-x}O₂ with *x* ranging from 0.6 to 0.8 [8,9]. It is well known that several factors influence the catalytic performance of supported Pd catalysts, such as the nature of the support, physicochemical properties of the metal particles, and metal-support interaction [1,3,10]. Among these factors, the configuration of the noble metal particles and noble metal-support interaction are considered to be two important factors affecting the amount and nature of the active sites [11]. Wang et al. [12,13] reported the effect of rare earth element (La, Nd, Pr, Sm and Y) doping on the three-way catalytic performance of Pd/Ce_xZr_{1-x}O₂ catalyst and showed that the addition of La or Pr promoted the interaction between PdO_x species and Ce_xZr_{1-x}O₂, resulting in increased thermal stability and oxygen storage capacity (OSC). In addition, we have studied the effects of CeO₂-ZrO₂ presence

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in Pd/Al₂O₃ catalysts on the redox behavior of PdO_x and their combustion activity [14]. The interaction between Ce-Zr and PdO_x controlled the growth of PdO_x particles and inhibited the decomposition of PdO to Pd⁰, and the reoxidation ability of Pd⁰ to PdO was greatly improved. Therefore, it increased thermal stability and the catalytic performance of the Pd/Ce-Zr/Al₂O₃ catalyst for methane combustion. Owing to the complexity of the large number of chemical reactions of TWCs, some arguments exist with regard to both the best configuration of the noble metal particle and the noble metal-support interaction.

The nature of the noble metal precursor utilized in the preparation of the catalyst is also considered to affect the noble metal-support interaction. Baylet et al. [15] studied the influence of the Pd precursor on the activity for CH₄ combustion and reported that using Pd(acac)₂ as the metal precursor gave a higher dispersion (> 30%), smaller Pd particle size (< 3 nm) and better catalytic performance than when using Pd(NO₃)₂. Panprant et al. [16] investigated the effects of the Pd precursor on hydrogenation and reported that using PdCl₂ as a precursor led to smaller Pd particles (< 4.5 nm), higher dispersion (> 26%) and hydrogenation activity than the catalysts prepared with Pd(NO₃)₂ or Pd(OOCCH₃)₂ precursors. However, the mechanism and the interaction between Pd precursor and the support are still not clear, and need to be further studied. On the other hand, for different reactions, the configuration of the noble metal particle and the different interaction between metal and the support also have a different effect on the catalytic performance.

The scope of this paper is to investigate the effect of the configuration of the noble metal particle and the metal-support interaction on the catalytic performance of TWC in automobile emission control. Ce_{0.67}Zr_{0.33}O₂ supported Pd catalysts that used three different Pd precursors, H₂PdCl₄ (chlorine-containing), Pd(NO₃)₂, and Pd(NH₃)₄(NO₃)₂ (chlorine-free), were prepared by impregnation. Their physical and chemical properties were characterized by X-ray diffraction (XRD), CO chemisorption, X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), H₂-temperature program reduction (H₂-TPR) and in situ diffuse reflectance infrared transform spectroscopy (DRIFTS). These techniques helped acquire some insight into what improved the catalytic performance for HC, CO and NO_x conversion in automobile exhaust.

2. Experimental

2.1. Catalyst preparation

Ce_{0.67}Zr_{0.33}O₂ (CZ, *S*_{BET} = 111 m²/g) was prepared by the co-precipitation method [17]. Three Pd/Ce_{0.67}Zr_{0.33}O₂ catalysts with 1.0 wt% loading were prepared with CZ using H₂PdCl₄, Pd(NO₃)₂ and Pd(NH₃)₄(NO₃)₂ as metal precursor by incipient wetness impregnation at 30 °C. The samples were dried at 110 °C for 4 h and then calcined at 500 °C in air for 2 h. The sample prepared from the H₂PdCl₄ precursor was designated as Pd/CZ(Cl), and that prepared from Pd(NO₃)₂ and Pd(NH₃)₄(NO₃)₂ precursors were designated as Pd/CZ(NO) and

Pd/CZ(NH). TWCs are frequently exposed to very high temperature above 1000 °C in the application, which is the main reason resulting in decreased catalytic performance [18,19]. Therefore, the catalysts were also treated at 1000 °C for 4 h to get aged catalysts designated as Pd/CZ(Cl)-a, Pd/CZ(NO)-a and Pd/CZ(NH)-a, respectively.

2.2. Catalytic performance test

The three-way catalytic performance tests were carried out in a fixed bed continuous flow reactor at atmospheric pressure. 0.2 ml catalyst (0.3–0.45 mm, 0.276 g) was used. The reaction mixture containing NO (0.121%), NO₂ (0.034%), C₃H₆ (0.067%), C₃H₈ (0.033%), CO (0.748%), O₂ (0.745%) and balance Ar was fed to the reactor at a GHSV of 43000 h⁻¹. The total flow rate was 143 ml/min. The effluent gas was analyzed by an online Fourier transform infrared spectrophotometer (BRUKER EQ55) equipped with a multiple reflection transmission cell (Infrared Analysis Inc.; path length 10.0 m). All spectra were taken at a resolution of 2 cm⁻¹ using 128 scans [20].

2.3. Characterization techniques

XRD measurement was performed on an ARL X'TRA X-ray diffractometer (Thermo Electron Co.), operating at 40 kV and 40 mA with Ni-filtered Cu K_α radiation. The dispersion of Pd was calculated on the basis of CO chemisorption at room temperature [21–23] using a CHEMBET-3000 apparatus (Quantachrome Co.). The catalyst was first reduced under H₂. CO chemisorption experiments were also performed with a Nicolet 6700 FTIR fitted with a MCT detector following the same pretreatment. The spectrum was recorded after CO adsorption at 30 °C. The dispersion (*D*) and palladium particle size (*d*) were calculated as [9,21,22]:

$$D (\%) = 100 \times [(V_s \times f) / (C_s \times W_s \times 22414)] \times m \quad (1)$$

$$d (\text{nm}) = 6 \times 10^5 \times m / (\rho_{\text{Pd}} \times D \times S_{\text{Pd}}) \quad (2)$$

where *V_s* is the CO volume adsorbed (ml at STP), *f* is the stoichiometric factor (= 1), *C_s* is Pd metal content (wt%), *W_s* is the sample weight (g), *m* is the Pd atomic mass (106.42 g/mol), *D* is Pd metal dispersion (%), *n* is Avogadro's number (6.02 × 10²³), *S_{Pd}* is molar surface area of Pd assuming an equidistribution of the low index faces (*S* = 47780 m²/mol for Pd metal) and *ρ_{Pd}* is palladium density (12 g/cm³).

XPS analysis was performed on a Thermo ESCALAB 250 spectrometer with Al K_α radiation (1486.6 eV) operating at 150 W and with an energy pass of 20 eV. The surface charging effect was corrected for by fixing the C 1s peak at a binding energy of 284.8 eV. HRTEM analysis was carried out on a TECNAI G220 apparatus operated at 200 kV. XEDS analysis was used to record elemental maps to find the chemical composition. The sample for the HRTEM study was first dispersed in ethanol and deposited onto a perforated carbon film supported on a copper grid.

The oxygen storage capacity complete (OSCC) measurement was carried out using a CHEMBET-3000 apparatus (Quantachrome Co.). The sample (100 mg) was first reduced under H₂ (10 ml/min) at 550 °C for 60 min, and then cooled

down to 400 °C and flushed with He (30 ml/min) for 30 min. 0.15 ml of O₂ was pulsed into the sample bed every 5 min until no consumption of oxygen could be detected.

UV-Raman spectra were recorded on a UV-HR Raman spectrograph with a He-Gd laser of 325 nm excitation wavelength. It consisted of two data accumulation of 30 s with a resolution of 4 cm⁻¹. A frequency range of 100–1000 cm⁻¹ was observed. H₂-TPR experiments were carried out on a GC-1690 chromatography. Each sample (50 mg) was pretreated under N₂ (30 ml/min) at 200 °C for 30 min and then cooled down to -50 °C in liquid nitrogen. A flow of 5% H₂/Ar (40 ml/min) was then switched into the system, and the temperature was raised to 900 °C at a rate of 10 °C/min. The consumption of H₂ was measured by a thermal conductivity detector (TCD). The water formed during the program was absorbed with 5A molecular sieve. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were conducted on a Nicolet 6700 FTIR fitted with a MCT detector. The DRIFTS cell was fitted with CaF₂ windows and a heating cartridge that allowed samples to be heated to 500 °C. Spectra were collected at the resolution of 4 cm⁻¹ using 32 scans. Prior to the infrared measurement, the sample was pretreated with Ar at 450 °C for 0.5 h and then cooled down to 30 °C in order to remove contaminants. The composition of the feed stream was the same as the catalytic

performance test.

3. Results and discussion

3.1. Catalytic performance

Fig. 1 shows the conversion of HC, CO, NO and NO₂ as a function of reaction temperature under stoichiometric CO + NO_x + HC + O₂ flow over the fresh and aged catalysts. As shown in Fig. 1, among the fresh catalysts, the Pd/CZ(NO) catalyst exhibited the best catalytic performance for HC and CO elimination. The Pd/CZ(NH) catalyst exhibited good performance for NO and NO₂ elimination. The Pd/CZ(Cl) catalyst exhibited the worst catalytic performance. However, after the aging treatment, the Pd/CZ(Cl)-a catalyst exhibited the best catalytic performance for HC and NO₂ conversion. The catalytic performance of both the Pd/CZ(NO)-a and Pd/CZ(NH)-a catalysts decreased except for CO elimination. It is known that chlorine has a strong interaction with ceria and it is hard to remove it completely when H₂PdCl₄ is the metal precursor. The chlorine residual in the fresh catalyst is harmful to the catalytic performance, probably due to the formation of CeOCl, which can only be decomposed by an aging treatment [24,25]. This indicated that the catalytic performance of the Pd-supported catalysts could be affected by

Fig. 1. Conversion of HC (a), CO (b), NO (c) and NO₂ (d) as a function of reaction temperature under a stoichiometric CO + NO_x + HC + O₂ flow over fresh and aged catalysts.

the nature of the Pd precursor.

3.2. Pd dispersion and chemical state

Pd dispersion of the fresh and aged catalysts was determined by CO chemisorption at room temperature. The results are listed in Table 1. The amount of CO bonded to the CZ support is very small after the heat treatment compared with the large amount of CO chemisorbed on the Pd/CZ catalysts, and it can be ignored. From Table 1, we can see that the fresh catalysts exhibited high Pd dispersion, indicating that the PdO_x species were well dispersed on the CZ support. The Pd dispersion order was $\text{Pd/CZ(NH)} > \text{Pd/CZ(NO)} > \text{Pd/CZ(Cl)}$. During the preparation, the pH of the H_2PdCl_4 and $\text{Pd(NO}_3)_2$ precursor solution was 2, and that of the $\text{Pd(NH}_3)_4(\text{NO}_3)_2$ precursor solution was 6. As studied by Kuno [26], the isoelectric point is in a range from 3.8 to 5.0 when the molar ratio Ce/Zr ranged from 3/7 to 7/3. The CZ support has a positive charge in the H_2PdCl_4 and $\text{Pd(NO}_3)_2$ precursor solution, and a slight negative charge in the $\text{Pd(NH}_3)_4(\text{NO}_3)_2$ precursor solution. In the three precursor solutions, Pd species existed as PdCl_4^{2-} , Pd^{2+} , and $\text{Pd(NH}_3)_4^{4+}$, respectively. The electrostatic interaction between PdCl_4^{2-} and the CZ support is stronger. Besides this, the strong interaction between chlorine and ceria also inhibited the activation of active PdO_x species and redispersion of PdO_x species by calcination at 500 °C. Therefore the fresh catalyst prepared with the H_2PdCl_4 precursor showed low dispersion. Compared to Pd^{2+} , $\text{Pd(NH}_3)_4^{2+}$ ions has a steric hindrance effect which helps to keep Pd isolated from each other, resulting in the Pd/CZ(NH) catalyst showing a better Pd dispersion than Pd/CZ(NO) . The particle size order was $\text{Pd/CZ(NH)} < \text{Pd/CZ(NO)} < \text{Pd/CZ(Cl)}$. For the aged catalysts, the Pd dispersion order was $\text{Pd/CZ(Cl)-a} \approx \text{Pd/CZ(NH)-a} > \text{Pd/CZ(NO)-a}$, and the mean particle size of Pd

Table 1

CO chemisorption quantity, dispersion, particle size of Pd and CO adsorption quantity of the three CO-Pd⁰ species over the fresh and aged catalysts.

Catalyst	n_{CO}^a ($\mu\text{mol/g}_{\text{cat}}$)	D^b (%)	D^c (nm)	n_{CO} of atop, bridge, 3-fold CO-Pd ⁰ species ^d ($\mu\text{mol/g}_{\text{cat}}$)
Pd/CZ(Cl)	17.7	20.1	5.5	4.8, 3.3, 9.6
Pd/CZ(NO)	23.0	24.5	4.5	13.1, 3.6, 6.3
Pd/CZ(NH)	37.4	39.8	2.8	12.0, 8.1, 17.3
Pd/CZ(Cl)-a	7.6	8.6	12.9	3.7, 1.2, 2.7
Pd/CZ(NO)-a	5.9	6.3	17.7	2.7, 1.1, 2.1
Pd/CZ(NH)-a	5.4	5.7	19.5	3.1, 0.7, 1.6

^a Amount of CO chemisorbed on Pd surface. ^b Pd dispersion determined by CO chemisorption. ^c Mean particle size calculated from Pd dispersion.

^d Calculated from the ratio of top/bridge/3-fold CO-Pd⁰ species and total CO chemisorption quantity.

in Pd/CZ(Cl)-a catalyst was smaller than in the other two catalysts. According to the catalytic performance test, Pd/CZ(NH) and Pd/CZ(NO) showed better catalytic performance for CO, HC, and NO_x conversion than the Pd/CZ(Cl) catalyst, but the Pd/CZ(Cl) catalyst lost the least catalytic activity after the aging treatment. This indicated that highly dispersed PdO_x species play a role in CO, HC and NO_x conversion. However, the CO conversion is significantly promoted by oxygen-storage materials and influenced by the OSC of the catalyst [27]. It is not only the configuration of the PdO_x particles on the surface of support but also the noble metal-support interaction that play an important role in NO conversion [27]. In order to obtain more information about the configuration of the PdO_x particles, the XRD, HRTEM, IR, and XPS results of the catalysts were analyzed.

HRTEM images of the fresh and aged catalysts are shown in Fig. 2. With all the fresh catalysts, only the CZ oxide was observed with an interplanar spacing of 0.31 nm corresponding to

Fig. 2. HRTEM images of Pd/CZ(Cl) (a), Pd/CZ(NO) (b), Pd/CZ(NH) (c), Pd/CZ(Cl)-a (d), Pd/CZ(NO)-a (e), and Pd/CZ(NH)-a (f) catalyst. The insets in (a), (b) and (c) are the corresponding STEM and EDS elemental mapping of Pd.

CeO₂ (111). The particle size was 5 nm. No PdO_x particle was found because Pd clusters are hard to observe owing to a lack of contrast with the support. In order to look at the distribution of PdO_x species on the fresh catalysts, we also measured the elemental mapping on the Pd/CZ(Cl) and Pd/CZ(NO) and Pd/CZ(NH) catalysts. The bright squares in the insets of Fig. 2(a–c) were attributed to high concentration PdO_x species, unlike the slight aggregation in the Pd/CZ(Cl) catalyst (shown in circle, Fig. 2(a)). The bright squares in the Pd/CZ(NO) and Pd/CZ(NH) catalysts were more isolated, meaning that the PdO_x species were uniformly distributed on the surface of support, in agreement with the result of the Pd dispersion measurement. Moreover, no CeOCl lattice fringes were determined in the Pd/CZ(Cl) catalyst, which was probably due to the low chlorine content from the H₂PdCl₄ precursor. After the aging treatment, based on the EDX spot spectrum taken from the region of the circled particle in Fig. 2(d), the lattice fringes with the interplanar spacing of 0.26 nm was determined to be associated with the (101) facet of PdO. PdO particles on the aged catalysts were observed as a result of the high aging temperature leading to a sintering of PdO. However, it was obvious that the Pd/CZ(Cl)-a catalyst showed a smaller diameter of PdO particles compared with the other catalysts, in agreement with the calculated Pd particle size order calculated from the Pd dispersion measurement. This was one of the reasons why the Pd/CZ(Cl) catalyst still has a good catalytic performance after the aging treatment.

In general, when calculating the dispersion, the stoichiometric factor f (Pd/CO) is assumed as 1 [21,22], while the adsorption of CO on the Pd metal sites has top, bridge and 3-fold forms [28–31], which depends on the configuration of the active components, in terms of the particle size and also particle shape. In order to clarify these aspects, the catalysts were examined by in situ DRIFTS. The DRIFTS spectra of CO chemisorption at 30 °C over the in situ reduced catalysts are shown in Fig. 3. The band at 2115–2025 cm⁻¹ corresponded to on-top carbonyl species chemisorbed on metallic Pd particles. Another band that appeared at 1980–1900 cm⁻¹ can be ascribed to carbonyl species chemisorbed on bridge sites of metallic Pd particles. A third carbonyl species that appeared as a low frequency

shoulder extending to 1900–1800 cm⁻¹. This shoulder can be ascribed to carbonyl species chemisorbed on threefold sites of metallic Pd particles [32]. The order of the total area of the carbonyl adsorption peaks in the fresh and aged catalysts was Pd/CZ(NH) > Pd/CZ(NO) > Pd/CZ(Cl), Pd/CZ(Cl)-a > Pd/CZ(NO)-a ≈ Pd/CZ(NH)-a, which agreed with metallic dispersion measurement results. From Table 1 and Fig. 3(a), we can find that the Pd/CZ(NO) catalyst showed an obvious increase in on-top CO-Pd⁰ species compared with Pd/CZ(Cl), suggesting that more small Pd_n clusters existed on the Pd/CZ(NO) catalyst surface. High dispersion and small clusters give more active sites and promote oxygen transfer, which is beneficial to CO and HC oxidation [33,34]. Therefore, the Pd/CZ(NO) catalyst exhibited the best oxidation of CO and HC activity at low temperatures. The Pd/CZ(NH) catalyst showed an obvious increase in bridge and 3-fold CO-Pd⁰ species, indicating that a larger amount of relatively big Pd_n clusters existed on the Pd/CZ(NH) catalyst surface. NO reduction is a structure sensitive reaction [27]. Therefore, abundant bigger Pd_n clusters facilitate the increase in NO reduction activity. As mentioned above, the important difference in the position of the CO absorption peak demonstrated clearly that the nature of the Pd precursor has a significant effect on the physicochemical properties of the PdO_x species on the surface of the support. In addition, compared with that of the fresh catalysts, from Table 1 and Fig. 3(b), it can be seen that both small Pd_n clusters and also the big Pd_n clusters on the aged catalyst surface were decreased, which indicated that the high temperature calculation led to the sintering of PdO_x species. However, the Pd/CZ(Cl)-a catalyst still had more small Pd_n clusters, which helped the Pd/CZ(Cl)-a catalyst keep a good catalytic performance for HC conversion.

The change of the electronic state of the Pd species was investigated by XPS. The Pd 3d XPS spectra of the catalysts before and after the aging treatment are shown in Fig. 4. The BE values of Pd 3d_{5/2} in these catalysts were 336.7–337.7 eV corresponding to the PdO state [31,35]. Compared with the Pd/CZ(Cl) catalyst, the peaks of the Pd/CZ(NO) and Pd/CZ(NH) catalysts were shifted to higher BEs. This was ascribed to the smaller particle size of PdO, in accord with the Kobayashi et al. [36]

Fig. 3. IR spectra of CO adsorbed on the fresh (a) and aged (b) Pd/CZ(Cl), Pd/CZ(NO) and Pd/CZ(NH) catalysts at 30 °C after the same pretreatment as the Pd dispersion measurement.

Fig. 4. Pd 3d XPS spectra for fresh (a) and aged (b) catalysts and Cl 2p spectra for fresh and aged Pd/CZ catalysts (c).

study that the interaction between small PdO_x particles and the support is stronger, improving the electron transfer from PdO_x particles to the CZ support and leading Pd to be in a more oxidized state. After the aging treatment, the BE of Pd $3d_{5/2}$ for Pd/CZ(NO)-a and Pd/CZ(NH)-a shifted to a lower value due to the sintering of PdO, while that for Pd/CZ(Cl)-a did not change much, indicating that the PdO_x species in Pd/CZ(Cl)-a still kept a relatively high dispersion, in agreement with the Pd dispersion measurement. Another reason may be that the CeOCl phase decomposed under the high temperature oxidizing conditions [25,37,38], resulting in more oxygen vacancies being formed on the CZ support and promoting the electron transfer from Pd to CZ. The Cl 2p XPS spectra of the fresh and aged Pd/CZ(Cl) catalysts (Fig. 4 (c)) also showed the exist of Cl species on the Pd/CZ(Cl) catalyst, while no Cl peak was detected for the Pd/CZ(Cl)-a catalyst.

According to the analysis above, there were more small Pd_n clusters on the Pd/CZ(NO) catalyst prepared with $\text{Pd}(\text{NO}_3)_2$ as the precursor, leading to a stronger interaction between the small PdO_x particles and support, which kept Pd in a more oxidized state and promoted the oxidation conversion of HC and CO. For the Pd/CZ(NH) catalyst, the higher Pd dispersion and abundant bigger Pd_n clusters resulted in good performance for NO and NO_2 elimination. The Pd/CZ(Cl) catalyst exhibited a low catalytic activity due to the relatively low Pd dispersion, weak Pd-support interaction and stable CeOCl species inhibiting oxygen vacancy creation. However, it exhibited good thermal stability as a result of the residual chlorine species being removed after the aging treatment.

3.3. OSC and oxygen vacancies studies

OSC of the catalyst is regarded as one of the most important parameters in the application. Table 2 gives the OSC of the catalysts at 400 °C and shows that the OSC of the fresh samples was in the order of Pd/CZ(NO) > Pd/CZ(NH) > Pd/CZ(Cl), which were obviously higher than that (382 $\mu\text{mol O}_2/\text{g}$) for the CZ support, indicating that a PdO-support interaction promoted the back-spillover of oxygen between support and active PdO_x species [12,31]. The obviously increased OSC in the Pd/CZ(NO)

catalyst means a stronger PdO-support interaction. Thus, the Pd/CZ(NO) catalyst showed the highest catalytic activity for CO oxidation. After the aging treatment, a loss of OSC occurred due to the sintering of the support and highly dispersed PdO_x species, which resulted in the PdO-support interaction weakening. For the Pd/CZ(Cl)-a catalyst, the surface Cl was removed and new oxygen vacancies created after the aging treatment. Thus, the aged catalyst showed a similar OSC performance.

Generally speaking, the oxygen vacancy concentration in the CZ support is in accordance with the OSC performance. Therefore, Raman characterization of the fresh and aged catalysts was carried out. The result is shown in Fig. 5. The Raman band at 450 cm^{-1} was attributed to the F_{2g} vibration mode of the fluorite structure of CeO_2 . The band at 630 cm^{-1} was ascribed to the non-degenerate LO mode of ceria as a result of the relaxation of symmetry rules, which is related to oxygen vacancies or lattice defects in the ceria lattice [39–41]. Another weak band observed at 320 cm^{-1} can be ascribed to the displacement of oxygen atoms from their ideal fluorite lattice positions [42]. It is well known that the concentration of oxygen vacancies can be observed by the ratio of the peak areas of the bands at 450 (A_{450}) and 630 cm^{-1} (A_{630}). For the fresh catalysts, Pd/CZ(NO) exhibited the highest A_{630}/A_{450} , and the order of A_{630}/A_{450} for the three catalysts was Pd/CZ(NO) > Pd/CZ(NH) > Pd/CZ(Cl), which is in good agreement with their OSC values. The result indicated that the amount of oxygen vacancies in the catalysts was also strongly affected by the PdO-support interaction. The strong interaction between Pd and the support would promote the reduction of ceria at the Pd-CZ interface, which increases the oxygen vacancies concentration and OSC performance. After the aging treatment, the difference of A_{630}/A_{450} values in the catalysts became negligible. Thus, the aged catalysts have similar OSC performance. However, compared with fresh

Table 2
Oxygen storage capacity and A_{630}/A_{450} of fresh and aged catalysts.

Catalyst	OSC ($\mu\text{mol O}_2/\text{g}$)		A_{630}/A_{450}	
	Fresh	Aged	Fresh	Aged
Pd/CZ(Cl)	556	458	1.03	1.15
Pd/CZ(NO)	696	445	1.27	1.08
Pd/CZ(NH)	642	462	1.24	1.10

Fig. 5. UV-Raman spectra of the fresh and aged catalysts.

Pd/CZ(Cl), the A_{630}/A_{450} for the Pd/CZ(Cl)-a catalyst was slightly increased because the residual chlorine species that have a strong interaction with ceria was removed.

3.4. Redox properties studies

H₂-TPR is a convenient way to characterize the redox properties of the samples. The different dispersion state of the PdO_x species and interaction with the support has a large effect on the redox properties of the catalysts. The H₂-TPR results of the fresh and aged catalysts are shown in Fig. 6. We can see that the H₂-TPR profiles of the fresh catalysts showed two hydrogen consumption peaks (α and β) below 150 °C, which can be assigned to the reduction of PdO_x species highly dispersed on the surface of the support and stable PdO species having a strong interaction with support, respectively [6,43]. However, according to the calculation (using a standard CuO sample with a similar TPR procedure), the total H₂ consumption of peaks α and β in three catalysts were 541, 627, and 534 $\mu\text{mol/g}_{\text{cat}}$, respectively, much higher than the nominal value (94 $\mu\text{mol/g}_{\text{cat}}$).

These were too large to be reasonably assigned to the reduction of PdO_x, suggesting that the presence of Pd promoted the adsorption and spillover of hydrogen from the noble metal particles to the support due to the strong interaction between Pd and CZ, leading to interfacial Ce⁴⁺ reduction at low temperature [44,45]. In addition, a negative peak at 70 °C was observed for the catalysts, especially for the Pd/CZ(Cl) catalyst, which is generally attributed to the decomposition of palladium hydride [17,20]. The existence of large Pd particles favors the formation and decomposition of the PdH_x phase [16,46], and the larger Pd particles have the more obvious decomposition peak of palladium hydride. This indicated that PdO_x species with a large size existed on the Pd/CZ(Cl) catalyst. Several previous investigations have reported that the catalytic performance coincides with the redox properties of the active species [47,48]. However, in the three-way catalytic reaction system, the redox properties of the active Pd species are not the main reason for catalytic performance. According to the catalytic performance test, the Pd/CZ(Cl) catalyst exhibited the lowest catalytic activity of CO, HC, and NO_x conversion compared with Pd/CZ(NO) and Pd/CZ(NH), which may have a relationship with the chloride-based preparation that is extensively used in industrial synthesis. The residual chloride, low Pd dispersion, and weak Pd-support interaction led to poor catalytic performance for the Pd/CZ(Cl) catalyst.

Significant changes in the reduction characteristics occurred for the catalysts after the aging treatment in Fig. 6(b). The decomposition peaks of palladium hydride became more obvious and the intensity of the reduction peaks (α) at low temperature was weakened, implying that PdO_x species were sintered after aging. However, it is worth noting that after the aging treatment, the intensity of the reduction peaks (β) was obviously increased and the peaks shifted to higher temperature, which suggested that the PdO species on the surface of the CZ support can migrate and more stable PdO species having a strong interaction with the support were formed at the high temperature of 1000 °C. From Fig. 6(b), it can also be found that the temperature of the reduction β peak over Pd/CZ(Cl)-a was lower than that of the other two catalysts, and this may be one of the reasons why the Pd/CZ(Cl)-a catalyst has a better catalytic performance.

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

3.5. In situ DRIFTS studies

In order to find a potential relationship between the particular PdO_x species and catalytic behavior during the light off process, in situ DRIFTS studies under a stoichiometric $\text{HC-CO-NO}_x\text{-O}_2$ flow were performed. DRIFTS spectra obtained every 20 °C under reaction conditions over the Pd/CZ(Cl) , Pd/CZ(NO) and Pd/CZ(NH) catalysts are shown in Fig. 7. The bands in the region of 1800–2300 cm^{-1} can be attributed to NCO and carbonyls species adsorbed on different PdO_x sites [29–31,49]. Overlap of the CO(g) features, showing two symmetrical bands at 2120 and 2170 cm^{-1} , has been subtracted from all spectra. From Fig. 7(a), it can be seen that for the Pd/CZ(Cl) catalyst, the presence of carbonyl adsorbed on Pd^{2+} (2161 cm^{-1}) was observed from 30 to 110 °C, no band corresponding to carbonyl chemisorbed on Pd^+ or Pd^0 was observed below 130 °C. This indicated that oxidized Pd species dominated the surface of the Pd/CZ(Cl) catalyst. Weak features at 2071 and 1960 cm^{-1} that showed on-top and bridge carbonyls adsorbed on Pd^0 sites were observed at 150 and 170 °C. This means the initially present PdO species were partly converted to Pd^0 particles under reaction conditions. When the temperature was increased up to 190 °C, these bands disappeared due to decreasing CO coverage caused by CO desorption and increasing CO conversion, which agreed with the light-off temperature of CO conversion in the catalytic performance test. A new band at 2179 cm^{-1} was observed above 190 °C. This was attributed to NCO species formed by N–O dissociation and subsequent bonding with CO(g) on Pd^0 sites. The formation of

NCO species is an important path for NO reduction and usually the strong intensity of the band is regarded as a useful fingerprint for monitoring NO dissociation [27,30]. Moreover, it is interesting that a band at 2001 cm^{-1} was also observed when the reaction temperature was increased up to 230 °C. According to the results of $\text{H}_2\text{-TPR}$ and CO-DRIFTS , there were two kinds of PdO_x species dispersed on the catalysts, thus, the band may be also related to NCO species produced on another kind of Pd^0 sites. For the Pd/CZ(NO) and Pd/CZ(NH) catalysts as shown in Fig. 7(b) and (c), there were similar bands to the Pd/CZ(Cl) catalyst. But compared with the Pd/CZ(Cl) catalyst, initial oxidized PdO species on the Pd/CZ(NO) catalyst were more easily converted to Pd^0 particles under reaction conditions. Metallic Pd species appeared at 110 °C. For the Pd/CZ(NH) catalyst, oxidized Pd species, coexisting with metallic Pd species which showed the formation of top carbonyl (2089 cm^{-1}) and bridge carbonyl (1961 cm^{-1}) species, was present at the beginning of the reaction. The Pd^0 species may be formed by the autoreduction of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ ions after calcination at 500 °C, in agreement with Wen et al. [50] who reported that Pd^{2+} ions with ammine ligands will auto-reduce followed by oxidation. As Pd^0 species are the active sites for NO adsorption and dissociation, the appearance of Pd^0 at a lower reaction temperature helps to promote the reaction of CO and NO [30,49]. On the other hand, compared with other two catalysts, the NCO peak appeared from a lower temperature (170 °C) in Pd/CZ(NH) catalyst. The results are in agreement with that the Pd/CZ(NH) catalyst showed the best catalytic activity for NO_x reduction.

Fig. 7. DRIFTS spectra for fresh Pd/CZ(Cl) (a), Pd/CZ(NO) (b), and Pd/CZ(NH) (c) catalysts under a stoichiometric $\text{CO} + \text{NO}_x + \text{HC} + \text{O}_2$ flow for reaction from 30 to 400 °C (from bottom to top).

The bands in the region of 1100–1800 cm^{-1} were attributed to carbonate and nitrates/nitrites species adsorbed on the support. From Fig. 7(a), for the Pd/CZ(Cl) catalyst, the bands in the region of 1680–1460 and 1460–1200 cm^{-1} , which showed an increase in intensity with increasing reaction temperature from 110 $^{\circ}\text{C}$, were ascribed to nitrates in a variety of structures and configurations ranging from bridged, bidentate, and monodentate NO_3^- species adsorbed on CZ [51–53]. The nitrates species is formed by the oxidation of some bidentate nitrites by an activated O^* surface species and the reaction of an hydroxyl group on a Ce^{4+} cation with NO_2 , and the thermal stability of the nitrates adsorbed on zirconium sites is higher than that of nitrates adsorbed on Ce sites. The Pd/CZ(NO) and Pd/CZ(NH) catalysts showed similar feature bands to the Pd/CZ(Cl) catalyst. But compared with the Pd/CZ(Cl) catalyst, the former showed stronger intensity for the chelated, bridged, and bidentate nitrites species adsorbed on CZ from 30 $^{\circ}\text{C}$, which was formed by the reaction of an hydroxyl group on a $\text{Ce}^{4+}/\text{Zr}^{4+}$ cation and an oxygen vacancy linked to a Ce^{3+} cation with NO or NO_2 [48,49]. These results suggested that for the Pd/CZ(Cl) catalyst, the existence of CeOCl species inhibited the formation of hydroxyl groups and oxygen vacancy on the CZ surface [38,54], in agreement with the oxygen vacancy results from Raman spectroscopy.

4. Conclusions

Catalytic behavior of Pd/Ce_{0.67}Zr_{0.33}O₂ catalysts prepared with different Pd precursors (H_2PdCl_4 , $\text{Pd}(\text{NO}_3)_2$ and $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$) were investigated. The nature of the palladium precursor affected the nature and configuration of the noble metal particles, noble metal-support interaction and catalytic activity for HC, CO, and NO_x elimination. Among the fresh catalysts, the Pd/CZ(NO) catalyst exhibited the best catalytic performance for HC and CO elimination as a result of a higher OSC, strong metal-support interaction improving electron transfer from PdO_x particles to the CZ support, and more small Pd_n clusters and active sites on the Ce_{0.67}Zr_{0.33}O₂ surface. For the Pd/CZ(NH) catalyst, the higher Pd dispersion and more

bigger Pd_n clusters resulted in good performance for NO and NO_2 elimination. The Pd/CZ(Cl) catalyst exhibited low catalytic activity because of the relatively low Pd dispersion, weak Pd-support interaction and a strong interaction between Cl and ceria leading to the formation of stable CeOCl species and inhibiting oxygen vacancy creation. However, after an aging treatment, it exhibited good thermal stability as a result of residual chlorine species being removed and the interaction between PdO_x and support being promoted. In situ DRIFTS also showed that the initial PdO_x species on the Pd/CZ(NO) and Pd/CZ(Cl) catalysts existed in the form of an oxidized state, while Pd metal and oxide species coexisted on Pd/CZ(NH). Moreover, compared with the Pd/CZ(Cl) catalyst, the initial oxidized PdO species on the Pd/CZ(NO) catalyst were more easily converted to Pd^0 particles under reaction conditions, and the presence of the Pd^0 particles promoted an increase in NO reduction activity.

References

- [1] Rajasree R, Hoebink J H B J, Schouten J C. *J Catal*, 2004, 223: 36
- [2] Mazumder V, Sun S. *J Am Chem Soc*, 2009, 131: 4588
- [3] Yang M, Shen M Q, Wang J, Wen J, Zhao M W, Wang J, Wang W L. *J Phys Chem C*, 2009, 113: 12778
- [4] Cui Y J, He S N, Fang R M, Shi Z H, Gong M C, Chen Y Q. *Chin J Catal* (崔亚娟, 何胜楠, 方瑞梅, 史忠华, 龚茂初, 陈耀强. 催化学报), 2012, 33: 1020
- [5] Yang X, Yang L Y, Lin S Y, Zhou R X. *Chin J Catal* (阳雪, 杨林颜, 林嗣煜, 周仁贤. 催化学报), 2014, 35: 1267
- [6] Li G F, Wang Q Y, Zhao B, Shen M Q, Zhou R X. *J Hazard Mater*, 2011, 86: 911
- [7] Kondratenko E V, Sakamoto Y, Okumura K, Shinjoh H. *Appl Catal B*, 2009, 89: 476
- [8] Terribile D, Trovarelli A, Llorca J, de Leitenburg C, Dolcetti G. *Catal Today*, 1998, 43: 79
- [9] Boaro M, de Leitenburg C, Dolcetti G, Trovarelli A. *J Catal*, 2000, 193: 338
- [10] Xu X, Li Y, Gong Y T, Zhang P F, Li H R, Wang Y. *J Am Chem Soc*, 2012, 134: 16987
- [11] Feng J T, Ma X Y, He Y F, Evans D G, Li D Q. *Appl Catal A*, 2012, 413-414: 10

Graphical Abstract

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The effect of Pd precursor on Pd/Ce_{0.67}Zr_{0.33}O₂ catalysts for automotive emission control

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Pd/CZ(NO) and Pd/CZ(NH) catalysts showed different behavior for HC, CO and NO_x elimination due to the presence of small or big Pd_n clusters. A Pd/CZ(Cl) catalyst showed low catalytic activity due to poor Pd dispersion and trace amounts of CeOCl that inhibited oxygen vacancy creation.

- [12] Wang Q Y, Li G F, Zhao B, Zhou R X. *Appl Catal B*, 2010, 100: 516
- [13] Wang Q Y, Li G F, Zhao B, Zhou R X. *Fuel*, 2011, 90: 3047
- [14] Zhou R, Zhao B, Yue B H. *Appl Surf Sci*, 2008, 254: 4701
- [15] Baylet A, Royer S, Marécot P, Tatibouët J M, Duprez D. *Appl Catal B*, 2008, 81: 88
- [16] Panpranot J, Tangjitwattakorn O, Praserttham P, Goodwin J G. *Appl Catal A*, 2005, 292: 322
- [17] Zhao B, Li G F, Ge C H, Wang Q Y, Zhou R X. *Appl Catal B*, 2010, 96: 338
- [18] Fornasiero P, Dimonte R, Rao G R, Kaspar J, Meriani S, Trovarelli A, Graziani M. *J Catal*, 1995, 151: 168
- [19] Suhonen S, Valden M, Hietikko M, Laitinen R, Savimäki A, Harkonen M. *Appl Catal A*, 2001, 218: 151
- [20] Wang Q Y, Li G F, Zhao B, Zhou R X. *J Hazard Mater*, 2011, 189: 150
- [21] Kang S B, Han S J, Nam S B, Nam I S, Cho B K, Kim C H, Oh S H. *Chem Eng J*, 2012, 207–208: 117
- [22] Kang S B, Kwon H J, Nam I S, Song Y I, Oh S H. *Ind Eng Chem Res*, 2011, 50: 5499
- [23] Takeguchi T, Manabe S, Kikuchi R, Eguchi K, Kanazawa T, Matsumoto S, Ueda W. *Appl Catal A*, 2005, 293: 91
- [24] Kępiński L, Okal J. *J Catal*, 2000, 192: 48
- [25] Fajardie F, Tempere J F, Manoli J M, Djega-Mariadassou G, Blanchard G. *J Chem Soc, Faraday Trans*, 1998, 94: 3727
- [26] Kuno O. US Patent 7384888 B2. 2008
- [27] Fernández-García M, Iglesias-Juez A, Martínez-Arias A, Hungria A B, Anderson J A, Conesa J C, Soria J. *J Catal*, 2004, 221: 594
- [28] Monteiro R S, Dieguez L C, Schmal M. *Catal Today*, 2001, 65: 77
- [29] Fernández-García M, Martínez-Arias A, Iglesias-Juez A, Hungria A B, Anderson J A, Conesa J C, Soria J. *Appl Catal B*, 2001, 31: 39
- [30] Martínez-Arias A, Hungria A B, Fernández-García M, Iglesias-Juez A, Anderson J A, Conesa J C. *J Catal*, 2004, 221: 85
- [31] Shen M Q, Yang M, Wang J, Wen J, Zhao M W, Wang W L. *J Phys Chem C*, 2009, 113: 3212
- [32] Royer S, Duprez D. *ChemCatChem*, 2011, 3: 24
- [33] Kane M D, Roberts F S, Anderson S L. *Faraday Discuss*, 2013, 162: 323
- [34] Shen M Q, Wei G X, Yang H M, Wang J, Wang X Q. *Fuel*, 2013, 103: 869
- [35] Hinokuma S, Fujii H, Okamoto M, Ikeue K, Machida M. *Chem Mater*, 2010, 22: 6183
- [36] Kobayashi T, Yamada T, Kayano K. *Appl Catal B*, 2001, 30: 287
- [37] Barrabes N, Föttinger K, Llorca J, Dafinov A, Medina F, Sa J, Hardacre C, Rupprechter G. *J Phys Chem C*, 2010, 114: 17675
- [38] Fallah J E, Boujana S, Dexpert H, Kiennemann A, Majerus J, Touret O, Villain F, Normand F L. *J Phys Chem C*, 1994, 98: 5522
- [39] Li S P, Lu J Q, Fang P, Luo M F. *J Power Sources*, 2009, 193: 93
- [40] Pu Z Y, Lu J Q, Luo M F, Xie Y L. *J Phys Chem C*, 2007, 111: 18695
- [41] Luo M F, Yan Z L, Jin L Y. *J Mol Catal A*, 2006, 260: 157
- [42] Reddy B M, Reddy G K, Katta L. *J Mol Catal A*, 2010, 319: 52
- [43] Hickey N, Fornasiero P, Kašpar J, Gatica J M, Bernal S. *J Catal*, 2001, 200: 181
- [44] Fan J, Wu X D, Wu X D, Liang Q, Ran R, Weng D. *Appl Catal B*, 2008, 81: 38
- [45] He H, Dai H X, Ng L H, Wong K W, Au C T. *J Catal*, 2002, 206: 1
- [46] Ferrer V, Moronta A, Sánchez J, Solano R, Bernal S, Finol D. *Catal Today*, 2005, 107–108: 487
- [47] Domingos D, Rodrigues L M T S, Frety R, Brandao S T. *Combust Sci Technol*, 2014, 186: 518
- [48] Lin W, Zhu Y X, Wu N Z, Xie Y C, Murwani I, Kemnitz E. *Appl Catal B*, 2004, 50: 59
- [49] Martínez-Arias A, Fernández-García M, Iglesias-Juez A, Hungria A B, Anderson J A, Conesa J C, Soria J. *Appl Catal B*, 2001, 31: 51
- [50] Wen B, Jia J, Sachtler W M H. *J Phys Chem B*, 2002, 106: 7520
- [51] Martínez-Arias A, Fernández-García M, Hungria A B, Iglesias-Juez A, Duncan K, Smith R, Anderson J A, Conesa J C, Soria J. *J Catal*, 2001, 204: 238
- [52] Atribak I, Azambre B, Bueno López A, García-García A. *Appl Catal B*, 2009, 92: 126
- [53] Azambre B, Atribak I, Bueno-Lopez A, Garcia-Garcia A. *J Phys Chem C*, 2010, 114: 13300
- [54] Huang Y Q, Wang A Q, Li L, Wang X D, Zhang T. *Catal Commun*, 2010, 11: 1090

钯前驱体对汽车尾气处理Pd/Ce_{0.67}Zr_{0.33}O₂催化剂催化性能的影响

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摘要: 分别以Pd(NO₃)₂, Pd(NH₃)₄(NO₃)₂和H₂PdCl₄为钯前驱体制备了Pd/Ce_{0.67}Zr_{0.33}O₂ (CZ)催化剂。以硝酸钯为钯前驱体制得的Pd/CZ(NO)催化剂具有较高的储氧量, 存在较多的小的钯簇, 其钯与载体间相互作用较强, 因此在三种新鲜催化剂中对HC和CO的消除表现出了最好的催化活性。以硝酸四氨钯为钯前驱体制得的Pd/CZ(NH)催化剂具有较高的钯分散度, 存在较多的大钯簇, 同时存在金属态和氧化态的钯, 从而对NO和NO₂的消除表现出了较好的催化活性。以氯钯酸为钯前驱体制得的Pd/CZ(Cl)催化剂由于钯分散度较小, 钯与载体间作用较弱, 存在的CeOCl抑制了氧空穴的生成, 因此对各种反应物的催化活性都较低。但Pd/CZ(Cl)催化剂表现出了较好的热稳定性, 这是由于老化处理消除了残余的氯物种并且促进了钯与载体间的作用。

关键词: 钯前驱体; 三效催化剂; 金属载体间相互作用; 起燃催化活性

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