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Zr掺杂对PdO/Ce_{1-x}Pd_xO_{2-δ}催化剂CO和CH₄催化氧化的影响

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摘要: 采用溶液燃烧法制备出PdO/Ce_{1-x}Pd_xO_{2-δ} (PdO/CP)和PdO/Ce_{1-x-y}Pd_xZr_yO_{2-δ} (PdO/CPZ)催化剂, 通过硝酸处理去除催化剂表面的PdO物种得到对应的Ce_{1-x}Pd_xO_{2-δ} (CP)和Ce_{1-x-y}Pd_xZr_yO_{2-δ} (CPZ)催化剂。考究四种催化剂(PdO/CP、PdO/CPZ、CP、CPZ)对CO和CH₄的氧化活性, 并计算得出表面PdO和Pdⁿ⁺物种的转化频率(TOF)。结果表明Zr的添加对PdO催化剂上CO和CH₄的催化氧化活性具有不同的影响。Zr的添加对PdO/CPZ和CPZ催化剂的CO催化活性具有明显的促进作用, 前者归因于PdO/CPZ催化剂表面生成了更小颗粒的PdO粒子, 后者归因于CPZ催化剂中含有更多的氧空位。对于CH₄的催化氧化, Pdⁿ⁺物种起到关键的作用。由于Zr的掺杂导致CeO₂的晶格中Pd物种的含量减少, 致使PdO/CPZ催化剂和CPZ催化剂对CH₄氧化活性的降低。

关键词: 铈; 氧化铈; 氧空位; CO氧化; CH₄氧化

中图分类号: O643

Effects of Zr Addition on CO and CH₄ Catalytic Oxidation over PdO/Ce_{1-x}Pd_xO_{2-δ} Catalyst

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Abstract: PdO/Ce_{1-x}Pd_xO_{2-δ} (PdO/CP) and PdO/Ce_{1-x-y}Pd_xZr_yO_{2-δ} (PdO/CPZ) catalysts were prepared via a solution combustion method. The corresponding Ce_{1-x}Pd_xO_{2-δ} (CP) and Ce_{1-x-y}Pd_xZr_yO_{2-δ} (CPZ) catalysts were obtained by nitric acid treatment of the PdO/CP and PdO/CPZ catalysts to remove the surface PdO species. These catalysts were tested for CO and CH₄ catalytic oxidation. The turnover frequencies (TOFs) of surface PdO and Pdⁿ⁺ cations in the CP and CPZ solid solutions were calculated. The results showed that Zr addition in the PdO/CP catalyst had very different effects on CO and CH₄ oxidation. A significant improvement in CO oxidation activity was observed over the Zr-containing catalysts; this could be related to the formation of smaller PdO particles on the surface of the PdO/CPZ catalyst and a higher oxygen vacancy concentration in the CPZ solid solution. For CH₄ oxidation, Pdⁿ⁺ cations in the solid solution play a key role in the catalytic oxidation process. The penetration of Zr⁴⁺ cations into the CeO₂ lattice decreased the amount of Pd²⁺ cations in the CPZ solid solution and thus inhibited the activities of the Zr-containing catalysts (PdO/CPZ and CPZ) for CH₄ oxidation.

Key Words: Zr; PdO; Oxygen vacancy; CO oxidation; CH₄ oxidation

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1 Introduction

CeO₂-based materials have been widely applied in catalysis, such as three-way catalysts (TWCs) for exhaust gas treatment from automobiles¹, solid oxide fuel cells^{2,3}, water-gas shift reaction⁴, and catalytic oxidation of CO and hydrocarbons^{5,6}. For each of these applications, the utilization of CeO₂ is motivated by its ability to store and release oxygen or easily transition between each oxidation states^{7,8}. Doping of ceria with different cations, such as Fe, Co, Ni, Cu, Zr, La, Pd, Pt, Pr, Y, Gd, Sn^{9–14}, could improve the oxygen storage-release capacity (OSC) or the redox properties and thus enhancing the catalytic activities of ceria. The enhanced OSC of ceria can be attributed to the substitution of isovalent and aliovalent metal ion in CeO₂, in the form of solid solutions Ce_{1-x}Cu_xO₂¹⁵, Ce_{1-x}Pd_xO₂ and Ce_{1-x}Pt_xO₂¹⁶, Ce_{1-x}Zr_xO₂¹⁷, Ce_{1-x}Sn_xO₂¹⁸, Ce_{1-x}Y_xO₂¹⁹. It is generally accepted that oxygen storage capacity is related to the oxygen vacancy formation on reduced CeO₂²⁰. Among the dopant, Zr-doped CeO₂ materials have been extensively studied. The substitution of Zr into CeO₂ lattice results in the formation of Ce_{1-x}Zr_xO₂ solid solution and greater redox properties, oxygen store capacity and thermal stability compared to pure CeO₂^{21–23}. Due to the remarkable redox properties, the CeO₂ and Zr-doped CeO₂ materials have been widely used as promising supports for catalysts. For example, Ce_{1-x}Zr_xO₂ solid solution supported Pd or Pt catalysts are applied in three-way catalysts for treating automobile exhaust gas²⁴, methane combustion²⁵, and water gas shift reaction²⁶.

CO and CH₄ oxidation have attracted much attention in the field of the eliminating of vehicle exhaust and volatile organic compounds (VOCs) in recent years^{27,28}. It is generally accepted that the substitution of dopant into the CeO₂ lattice could change the redox property and the catalytic properties of the catalysts. Isolated encapsulated Pd metal in ceria as a result of a strong metal-support interaction was reported in early studies of noble-metal/ceria systems²⁹. Boronin *et al.*²⁹ synthesized palladium catalysts supported on nanosized CeO₂ supports by different methods and found that the catalysts showed high low-temperature activity (LTA) in CO oxidation. Gulyaev *et al.*³⁰ investigated the correlation between the activity of the Pd/CeO₂ catalysts and the states of the palladium species. The results showed that palladium species is represented by two surface phases: a solid solution of Pd₂Ce_{1-x}O_{2-θ} and palladium (PdO), clusters. These surface phases were oxidized or reduced depending on the reaction conditions and the gas medium composition. Mayernick and coworkers compared surface reduction on pure CeO₂ (111), (110), and (100) surface and surfaces with Zr or Pd substituted in Ce lattice positions by density functional theory for CH₄ oxidation reaction and found that Pd-substituted surface was more reducible than the Zr-substituted surface³¹.

Another possible way to change the activity of PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst for CO or CH₄ oxidation is modification by two or more promoters. Baidya *et al.*³² synthesized nano-Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-δ} solid solution by solution combustion method. The results showed that synergistic interaction of Pd with Ti/Ce is very strong because

of ionic substitution. The reducibility of Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-δ} is about 5 times higher compared to that of Ce_{0.98}Pd_{0.02}O_{2-δ} below 140 °C and the lattice oxygen can be more easily exchanged from Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-δ} compared to Ce_{0.98}Pd_{0.02}O_{2-δ} in CO oxidation reaction. Singh and coworkers³³ prepared nanocrystalline Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815} material of ~4 nm sizes and found that due to the interaction of redox potentials of Pd^{2+/0} (0.89 V) and Fe^{3+/2+} (0.77 V) with Ce^{4+/3+} (1.61 V), Pd ion accelerates the electron transfer from Fe²⁺ to Ce⁴⁺ in Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}, making it a high oxygen storage material as well as a highly active catalyst for CO oxidation. Solid solutions based on PdO/CeO₂ of composition Ce_{0.99}Pd_{0.01}O_{2-δ} or Ce_{0.76}Zr_{0.19}Pd_{0.05}O_{2-δ} were reported more recently and found to be active in CO and CH₄ oxidation^{34,35}. It has been reported that the catalytic activity of CO on the Pd catalysts supported on commercial Ce-Zr solid solution (Pd/CZ) was effected by calcination temperature and hydrothermal treatment. For CO oxidation, the activity of either fresh or aged Pd/CZ catalysts decreased with the elevating of calcination temperature of CZ support³⁶. The research of Jin *et al.*³⁷ showed that Zr-embedded oxides promoted the methane catalytic activity on oxygen consumption due to the interaction between Zr and Pd at the interface, dispersing and stabilizing Pd particles on the catalyst surface. Also, Yang *et al.*³⁸ found that the molar ratios of Ce/Zr also play an important role in the catalytic activity and stability of the catalysis, their result shows that Pd/CZP catalysts with Ce/Zr molar ratio of 2 : 1 to 1 : 2 exhibit good thermal stability. These previous works suggest that addition of metal ion into the Ce_{1-x}Pd_xO_{2-δ} solid solution may accelerate the reaction.

The objective of this work was to investigate the effect of Zr addition to the PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst for CO and CH₄ oxidation. A series of PdO/CP, PdO/CPZ, CP, and CPZ catalysts were prepared using the solution combustion method and comprehensive study of their catalytic performances for CO and CH₄ oxidation was conducted. Various characterizations were performed to correlate the catalytic behaviors with the natures of the catalysts. Based on these examinations, the effect of Zr addition to the PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst for the CO and CH₄ oxidation was discussed. In addition, this study presents a method to calculate the turnover frequencies (TOFs) of surface PdO species for CO oxidation and Pd²⁺ cations in the CP and CPZ solid solution for CH₄ oxidation based on the amount of active sites measured by CO chemisorption and the percentage of Pd²⁺ cations exposed on the surface of CP or CPZ solid solution, correspondingly.

2 Experimental

2.1 Catalyst preparation

A PdO/Ce_{1-x-y}Pd_xZr_yO_{2-δ} catalyst was prepared by a solution combustion method³⁹. A detailed process was as follows: 20.74 g of (NH₄)₂Ce(NO₃)₆ (37.83 mmol, AR) was dissolved in 14 mL of deionized water in a porcelain crucible with 100 mL capacity. Pd(NO₃)₂ (0.97 mmol, AR) aqueous solution, Zr(NO₃)₄ · 5H₂O (9.70 mmol, AR) and C₂H₅NO₂ (125.62 mmol, 99.0%, AR) were added to the Ce-containing solution. The mixture contained

(NH₄)₂Ce(NO₃)₆, Pd(NO₃)₂, Zr(NO₃)₄, and C₂H₅NO₂ with a molar ratio of 0.78 : 0.02 : 0.20 : 2.59. Then, the porcelain crucible was introduced into a muffle furnace maintained at 350 °C. Initially the solution boiled with frothing, foaming and ignited to burn with a flame yielding a solid product. The solid was calcined at 800 °C in air for 4 h, and the resulting sample was denoted as PdO/CPZ.

A PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst was prepared by the same method as the PdO/Ce_{1-x-y}Pd_xZr_yO_{2-δ} catalyst. The molar ratio of (NH₄)₂Ce(NO₃)₆, Pd(NO₃)₂, and C₂H₅NO₂ was 0.98 : 0.02 : 2.59. The sample was denoted as PdO/CP.

A Ce_{1-x-y}Pd_xZr_yO_{2-δ} catalyst was obtained by treating the PdO/Ce_{1-x-y}Pd_xZr_yO_{2-δ} with nitric acid. 1 g of the PdO/Ce_{1-x-y}Pd_xZr_yO_{2-δ} catalyst was immersed in a hot concentrated nitric acid (15 mL, 50% (φ, volume fraction)) for 1 h then filtered. The above process was repeated for three times. Finally, the obtained solid was washed with plenty of deionized water to remove the residual nitric acid and dried at 90 °C overnight. The dried sample was characterized by Fourier transform infrared (FTIR) spectroscopy to confirm that there was no residual NO₃⁻ in the sample. The sample was denoted as CPZ.

A Ce_{1-x}Pd_xO_{2-δ} catalyst was obtained by the same method as the Ce_{1-x-y}Pd_xZr_yO_{2-δ} catalyst by treating the PdO/Ce_{1-x}Pd_xO_{2-δ} with nitric acid. The sample was denoted as CP.

The pure CeO₂ was also prepared in a similar manner as the PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst and calcined in air at 800 °C for 4 h.

2.2 Characterizations

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO MPD powder diffractometer using Cu K_α radiation (λ = 0.1542 nm). The working voltage was 40 kV and the working current was 40 mA. The patterns were collected in a 2θ range from 10° to 110°. The mean crystallite size was determined from line-broadening measurements on the (111) peak of CeO₂, using the Scherrer equation: $D = K\lambda/\beta\cos\theta$, where λ is the synchrotron wavelength (λ = 0.1541 nm), K is the particle shape factor, taken as 0.94 for spherical particles, β is the full-width at half maximum height (FWHM) in radians. The β values were carefully determined by a least-square fit of a Gaussian function. The lattice parameter was determined by the Rietveld method using JADE 6.5 software.

Specific surface areas (S_{BET}) of the catalysts were measured from a multipoint Brunauer-Emmett-Teller (BET) analysis of the nitrogen adsorption and desorption isotherms at 77 K, recorded on a Quantachrome Autosorb-1 apparatus. Before measurement, the sample was dried at 100 °C for 4 h under vacuum.

Elemental compositions of the catalysts were determined by X-ray fluorescence (XRF) analysis, on an ARL ADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The results were analyzed using UniQuant non-standard sample quantitative analysis software.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of CO chemisorption over the samples were recorded using a Nicolet 6700 spectrometer equipped with a MCT detector and a diffuse reflectance cell (Harrick CHC-CHA-3), with a resolution

of 4 cm⁻¹. An accumulation of 32 scans was used for collecting the spectra. About 20 mg of the catalyst was placed in the cell and pretreated at 300 °C for 1 h in a flow of Ar (30 mL · min⁻¹) in order to remove water and carbonate in the catalyst. Subsequently, the system was cooled down to 30 °C and the background spectrum was recorded. After the introduction of the gas mixture (1% (φ) CO in Ar, 30 mL · min⁻¹ for 30 min, the catalyst was purged with Ar for 30 min to remove the gaseous and physisorbed CO, and then a spectrum was collected.

Raman spectra of the samples were recorded on a Renishaw RM1000 with a confocal microprobe Raman system using an excitation laser line of 325 nm, in a range from 350 to 1000 cm⁻¹.

Reducibility of the catalysts was measured by the hydrogen temperature-programmed reduction (H₂-TPR) technique. 50 mg of the sample was placed in a quartz reactor connected to a homemade TPR apparatus. The catalyst was pretreated with high purity nitrogen (N₂) at 200 °C for 1 h to remove the water in the catalyst and cooled down to 30 °C. Subsequently, the reactor was heated from 30 to 800 °C with a heating rate of 10 °C min⁻¹ in a reducing atmosphere of mixed H₂ (5% (φ)) and N₂ (95% (φ)) with a total flow rate of 30 mL · min⁻¹. The amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD), calibrated by using a known amount of pure CuO powder. The water produced in TPR was trapped on a 0.5 nm molecular sieve.

The amount of CO chemisorption and the dispersion of Pd were carried out on a Quantachrome CHEMBET-3000 instrument. The sample was placed in a quartz U-tube and high-purity He (99.999%) was used as the carrier gas. The samples were reduced in a H₂-N₂ mixture (5% (φ) H₂, 30 mL · min⁻¹) stream at 300 °C for 1 h, and purged with He for 1 h to remove residual H₂ and N₂, then cooled down to 30 °C in a pure He flow (30 mL · min⁻¹). The pulses of CO were fed into the stream of carrier gas with a precision analytical syringe.

2.3 Catalytic testing

CO and CH₄ oxidation were carried out in a quartz tubular (i.d. = 6 mm) fixed-bed reactor under atmospheric pressure. 200 mg of the catalyst (80–100 mesh) was loaded in the reactor and the reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed. The total flow rate was 40 mL · min⁻¹, corresponding to a space velocity of 12000 mL · g⁻¹ · h⁻¹. The catalyst was directly exposed to the reaction without any pretreatment. For CO oxidation, a mixture of 1% (φ) CO and 1% (φ) O₂ balanced by N₂ was introduced as the reactants. Every temperature was stabilized for 30 min before analysis. The CO concentration in the reactor effluent was analyzed using an Agilent 6850 gas chromatograph equipped with a TCD and an HP PLOT (30 m × 0.32 mm × 12 μm) column. For CH₄ oxidation, the reactants contained a mixture of 0.5% (φ) CH₄, 3% (φ) O₂, and 96.5% (φ) N₂. The CH₄ concentration was analyzed using a Shimadzu GC-14 gas chromatograph equipped with a FID detector and a Supelcowax-10 (30 m × 0.25 mm × 0.25 μm) column.

Conversion of CO was calculated as follows:

$$\text{CO conversion} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%$$

where, $[\text{CO}]_{\text{in}}$ is the CO concentrations in the feed stream, $[\text{CO}]_{\text{out}}$ is the CO concentrations in the effluent gases.

Conversion of CH_4 was calculated as follows:

$$\text{CH}_4 \text{ conversion} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100\%$$

where, $[\text{CH}_4]_{\text{in}}$ is the CH_4 concentrations in the feed stream, $[\text{CH}_4]_{\text{out}}$ is the CH_4 concentrations in the effluent gases.

The turnover frequencies (TOFs) of PdO on the surface of PdO/CP and PdO/CPZ catalysts for CO oxidation is calculated based on the conversion of CO and the amount of active sites measured by CO chemisorption. Assuming the number of CO molecules adsorbed on the PdO/CP and PdO/CPZ catalysts equals to the number of surface active sites. The TOFs were calculated as follows (Part I, Supporting Information):

$$\text{TOF}_{\text{PdO}} = \frac{F_{\text{CO}} \times X_{\text{CO}}}{N}$$

where, TOF_{PdO} is the TOF of free PdO species on the surface of PdO/CP or PdO/CPZ catalysts; F_{CO} is the flow rate of CO; X_{CO} is the CO conversion of PdO/CP or PdO/CPZ catalysts; N refers to the amount of active sites on the PdO/CP or PdO/CPZ catalysts.

The turnover frequencies (TOFs) of Pd^{n+} cations in the CP or CPZ solid solution for CH_4 oxidation is calculated based on the percentage of Pd^{n+} cations exposed in the CeO_2 crystal particle in CP or CPZ catalysts. Assuming that the CP and CPZ solid solution are well-proportioned and Pd^{n+} cations dispersed in the solid solution uniformly. The TOFs were calculated as follows (Part II, Supporting Information)

$$\text{TOF}_{\text{Pd}^{n+}} = \frac{F_{\text{CH}_4} \times X_{\text{CH}_4}}{N \times R}$$

where, $\text{TOF}_{\text{Pd}^{n+}}$ is the TOF of Pd^{n+} cations in the CP or CPZ solid solution; F_{CH_4} is the flow rate of CH_4 ; X_{CH_4} is the CH_4 conversion of CP or CPZ catalysts; N refers to the amount of Pd in the CP or CPZ solid solution; R is the percentage of Pd^{n+} cations exposed in the CeO_2 crystal particle in CP or CPZ catalysts.

3 Results

3.1 Structural characterization

Fig.1 shows the XRD patterns of the PdO/CP, PdO/CPZ, CP, CPZ, and CeO_2 catalysts. The strong characteristic peaks of the cubic CeO_2 phase at 28.5° and 47.5° are observed in all the catalysts. However, no diffraction peaks attributed to the PdO/Pd phase are observed, which may be due to the high dispersion of PdO or Pd species on the surface of the catalysts. For the PdO/

Fig.1 XRD patterns of PdO/CP, PdO/CPZ, CP, CPZ, and CeO_2 catalysts

CPZ and CPZ catalysts, weak peaks attributed to tetragonal ZrO_2 phase are detected, suggesting that some ZrO_2 species formed on the PdO/CPZ catalysts.

Table 1 lists Pd content, specific surface area, cell parameter, crystallite size, and PdO particle size of the catalysts. The Pd contents in the catalysts were evaluated by XRF technique. It was found that Pd contents in the PdO/CP and PdO/CPZ catalysts are 1.70% and 1.60% (w, mass fraction), respectively. After the nitric acid treatment, Pd contents in the CP and CPZ catalysts decreased to 1.50% (w) and 1.37% (w), respectively. This indicates that most of the Pd species penetrated in the CeO_2 lattice and very limited amount of surface PdO species left on the of the PdO/CP and PdO/CPZ catalysts. The lattice parameters of PdO/CP, PdO/CPZ, CPZ, and CP catalysts decrease slightly compared to that of pure CeO_2 (JCPDS No. 34-0394), indicating that some Pd^{n+} or Zr^{4+} cations incorporate into the ceria lattice to form the CP or CPZ solid solution. This is because the radii of Pd^{2+} (0.084 nm), Pd^{4+} (0.062 nm), and Zr^{4+} (0.080 nm) are smaller than that of Ce^{4+} (0.099 nm), leading to a decline in lattice parameter when Ce^{4+} ions are partially substituted by Pd^{n+} or Zr^{4+} cations to form the CP or CPZ solid solution. The formation of CP or CPZ solid solution is also confirmed by Raman spectroscopy.

In addition, the crystallite size of CeO_2 in PdO/CP and PdO/CPZ catalysts are 18.7 and 12.8 nm, which are smaller than that of pure CeO_2 (33.7 nm). This indicates that the formation of CP ($\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$) and CPZ ($\text{Ce}_{1-x-y}\text{Pd}_x\text{Zr}_y\text{O}_{2-\delta}$) solid solution inhibits the growth of CeO_2 crystallite. The nitric acid treated samples (CP and CPZ) have similar physical properties (surface area, lattice parameter, and crystallite size) as the corresponding PdO/CP and

Table 1 Specific surface area, cell parameter, crystallite sizes, Pd content, and Pd particle size of the catalysts

Catalyst	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	Cell parameter of CeO_2/nm	Crystal size of CeO_2/nm	Pd content/% ^a	Pd dispersion ^b	Pd particle size/nm ^c
PdO/CP	12.7	0.5406	18.7	1.70	0.62	1.8
CP	11.6	0.5407	18.3	1.50	—	—
PdO/CPZ	12.5	0.5404	12.8	1.65	0.93	1.2
CPZ	8.8	0.5405	12.9	1.37	—	—
CeO_2	3.3	0.5411	33.7	—	—	—

^adetermined by XRF technique; ^bcalculated based on CO chemisorption results; ^cassuming that $d(\text{nm}) = 1.12/D(\text{dispersion})^{40}$

PdO/CPZ catalysts, suggesting that the acid treatment hardly changes the structure of the sample. It also can be seen that the particle size of PdO species on the surface of PdO/CPZ and PdO/CP catalysts is quite small (< 2.0 nm), which is measured by CO chemisorption.

Fig.2 shows the H₂-TPR profiles of the catalysts. The peaks at 480–520 °C for all the catalysts could be assigned to the reduction of surface Ce⁴⁺ cations⁴¹. For the PdO/CP catalyst, the peak at 70 °C could be assigned to the reduction of surface PdO species⁴² and the peaks at 100 and 140 °C could be assigned to the reduction of Pd²⁺ cations in the CP solid solution. The reduction peak of PdO starts below 100 °C for the fresh catalyst, which may be related to the Pd/Ce interface consistent with the result of Fernández-García *et al.*⁴³. After the nitric acid treatment, the peaks of the CP catalyst at 230 and 268 °C could be assigned to the reduction of Pd²⁺ cations in the CP solid solution. Obviously, the reduction peak for the PdO/CP catalyst appeared at 100 °C while the reduction peak in the CP catalyst showed at 230 °C, which may be due to a typical hydrogen spillover effect of the surface PdO species⁴⁴. This is also confirmed by the fact that the PdO/CP and CP have similar peak areas (293 vs 234). For the PdO/CPZ catalyst, the strong peak at 100 °C could be assigned to the overlapped reduction of surface PdO species and Pd²⁺ cations in the CPZ solid solution. After the nitric acid treatment, the reduction peak at 100 °C shifts to a higher temperature. The peaks at 234 and 268 °C of the CPZ catalyst could be attributed to the reduction of the Pd²⁺ cations in the CPZ solid solution. The integrated areas of the TPR peaks of the CP and CPZ catalysts are also calculated as can be seen in Fig.2. The peak area of CPZ catalyst increases compared to that of CP catalyst. This may be due to the fact that Zr⁴⁺ cations penetrate into the CeO₂ lattice and thus increasing more “labile” or “active” oxygen in the catalysts.

Fig.3 shows the Raman spectra of the catalysts. It is found that the PdO/CP, PdO/CPZ, CP, and CPZ catalysts have three distinct bands at 460, 588, and 660 cm⁻¹. The bands at 460 and 588 cm⁻¹ could be ascribed to vibration mode of F_{2g} symmetry in the cubic lattice of CeO₂^{45,46} and defect-induced (D) mode (oxygen vacancies)^{47,48}, respectively. For the Pd-contained catalysts, a weak band

Fig.2 H₂-TPR profiles of the PdO/CP, PdO/CPZ, CP, CPZ, and CeO₂ catalysts

Fig.3 Raman spectra of the PdO/CP, PdO/CPZ, CP, CPZ, and CeO₂ catalysts

at 660 cm⁻¹ attributed to the vibration mode of Pd—O bond^{49,50}.

The peak areas of the bands at 460 and 588 cm⁻¹ were also calculated based on the results showed in Fig.3, which are denoted as A_{460} and A_{588} , respectively. The ratio of A_{588}/A_{460} reflects the oxygen vacancy concentration in the catalysts⁵¹. It is clear that the A_{588}/A_{460} value for PdO/CP, CP catalysts (1.4) is higher than that of CeO₂ (0.7). When introducing Zr to the catalyst, the A_{588}/A_{460} value (1.7) of the PdO/CPZ and CPZ catalysts is higher than those obtained catalysts. This may be due to the fact that Zr⁴⁺ cations penetrated into the CeO₂ lattice, resulting in a larger amount of oxygen vacancies created in the samples. This also suggests that the formation of CP and CPZ solid solution, which is in good agreement with the XRD results (Fig.1).

3.2 DRIFT spectra of CO chemisorption on the catalysts

Fig.4 shows the DRIFT spectra of CO chemisorption on the PdO/CP, PdO/CPZ, CP, CPZ, and CeO₂ catalysts. The band at 2085 cm⁻¹ is characteristic of the linear adsorption of CO on metallic Pd⁰ and the band in the region of 1850–1969 cm⁻¹ is attributed to the isolated bridged and compressed bridged ad-

Fig.4 *In situ* DRIFT spectra for CO chemisorption on PdO/CP, PdO/CPZ, CP, CPZ, and CeO₂ catalysts

sorption of CO on metallic Pd⁰⁵². However, no obvious bands are observed in the region of 1800–2300 cm⁻¹ for the CP and CPZ catalysts, indicating that PdO on the surface of PdO/CP and PdO/CPZ catalysts have been removed and the CO molecules can hardly chemisorb on the surface of CP and CPZ solid solution.

3.3 Catalytic activity

Fig.5 shows the catalytic activities of the PdO/CP, PdO/CPZ, CP, and CPZ catalysts for CO and CH₄ oxidation. For CO oxidation, the PdO/CPZ catalyst has the highest activity with a T_{50} (the temperature required for 50% conversion) of 97 °C, while that for PdO/CP catalyst is 125 °C. However, after the acid treatment, the activities of the CP and CPZ catalysts are much lower than that of the PdO/CP and PdO/CPZ catalysts. This may be due to the fact that the PdO species on the surface of PdO/CP and PdO/CPZ catalysts were removed and thus the activation of CO molecule became more difficult (Fig.5). On the contrary, the surface PdO species containing catalysts (PdO/CP and PdO/CPZ) showed lower activity for CH₄ oxidation than corresponding CP and CPZ catalysts. This indicates that surface PdO species inhibits the activity of the PdO/CP and PdO/CPZ catalysts for CH₄ oxidation. Thus, it can be concluded that the surface PdO species is not the active sites for CH₄ oxidation. Moreover, the PdO/CPZ catalyst shows a lower activity than that of PdO/CP catalysts, the CPZ catalyst also shows a lower activity than that of CP catalyst.

Table 2 lists the TOF of surface PdO for CO oxidation and TOF of surface Pd⁺⁺ cations for CH₄ oxidation. TOFs for CO oxidation are calculated based on the amount of CO adsorbed on the catalysts. TOFs for CH₄ oxidation are calculated based on the surface

Pd⁺⁺ cations exposed on CP and CPZ solid solution. This suggests that the Zr addition in the catalysts enhanced the activity of the catalysts for CO oxidation but suppressed the activity of the catalysts for CH₄ oxidation.

It can be seen that the TOF of surface PdO species on PdO/CPZ catalyst ($0.22 \times 10^{-2} \text{ s}^{-1}$) is much higher than that on the PdO/CP catalyst ($0.09 \times 10^{-2} \text{ s}^{-1}$) for CO oxidation, which is consistent with the activities of the catalysts. This could be ascribed that the addition of Zr promotes the formation of smaller PdO particles and oxygen vacancy on the surface of the PdO/CPZ catalyst. However, for the CH₄ oxidation, The Pd⁺⁺ cations in CP solid solution possess a higher TOF ($1.4 \times 10^{-2} \text{ s}^{-1}$) than that in the CPZ solid solution ($0.8 \times 10^{-2} \text{ s}^{-1}$). This suggests that the Zr addition in the catalysts suppressed the activity of the catalysts for CH₄ oxidation.

4 Discussion

4.1 Structural properties of catalysts

In this work, PdO/CP, PdO/CPZ, CP, and CPZ catalysts were prepared by a solution combustion method. Various techniques are employed in order to obtain structural and surface information of the catalysts. The results show that the PdO/CP contains surface PdO species and CP solid solution; the PdO/CPZ catalyst contains surface PdO, ZrO₂ species and CPZ solid solution. The formation of CP and CPZ solid solution is confirmed by Raman spectroscopy and cell parameters of catalysts derived from XRD results. The surface PdO species could be removed by acid treatment as confirmed by H₂-TPR and DRIFT. The remaining CP and CPZ solid solution keeps their structures, which are confirmed by XRD and Raman spectroscopy. In addition, the PdO species on the surface of PdO/CP and PdO/CPZ catalysts and Pd⁺⁺ cations in the CP and CPZ solid solution are quantitatively evaluated by XRF technique. The results reveal that the content of Pd⁺⁺ cations in the CP and CPZ solid solution is much higher than that on the surface of catalysts. Doping of Zr⁴⁺ cations can cause disorder in the fluorite structure of CeO₂ and then give rise to various changes in physicochemical properties, which leads to different effects of catalysts for CO and CH₄ oxidation.

4.2 Effect of Zr addition in the catalysts for CO oxidation

For CO oxidation, the activity of the PdO/CPZ catalyst is enhanced due to the Zr addition in the catalyst and the TOF of the PdO species on the surface of PdO/CPZ catalyst is 2.5 times as high as that of the PdO/CP catalyst. Due to the Zr⁴⁺ cations pen-

Fig.5 Catalytic activities of the catalysts for CO and CH₄ oxidation

Table 2 Amount of CO adsorption, conversion, TOF of surface PdO and Pd⁺⁺ cations exposed on the surface of CP and CPZ solid solution

Catalyst	$V_{\text{co}}/(\text{cm}^3 \cdot \text{g}^{-1})^a$	CO oxidation ^b		CH ₄ oxidation ^c	
		conversion/%	10^2 TOF/s^{-1}	conversion/%	10^2 TOF/s^{-1}
PdO/CP	2.1	5.5	0.09	6.5	—
PdO/CPZ	2.9	19.4	0.22	5.0	—
CP	0.0	—	—	15.2	1.4
CPZ	0.0	—	—	10.7	0.8

^aAmount of CO adsorbed on the PdO/CP or PdO/CPZ catalysts is based on CO chemisorption technique. ^bReaction temperature is 80 °C for PdO/CP and PdO/CPZ catalysts. ^cReaction temperature is 350 °C for CP and CPZ catalysts.

etrated into the CeO₂ lattice, more Pd species left on the surface of the PdO/CPZ catalyst in the form of PdO species than that on the PdO/CP catalyst (Table S1, Supporting Information). The surface PdO species facilitate chemisorption and activation of CO molecules as can be seen in Fig.4. It has been generally recognized that the chemisorption of CO is important for the catalysts in CO oxidation, as the activation barrier of CO molecules could be significantly lowered¹⁵. Our previous work⁵³ showed that minute PdO species existing on the surface of Ce_{0.974}Pd_{0.026}O_{2-δ} mixed oxide prepared by solution-combustion method are responsible for high activity in low temperature CO oxidation. After the acid treatment, the activities of the CP and CPZ catalysts decreased greatly. This is due to the surface PdO species was removed and thus the activation of CO molecules became difficult (Fig.4). More significantly, it can be seen from Table 1 that the size of PdO particles decreases from 1.8 nm on the PdO/CP catalyst to 1.2 nm on the PdO/CPZ catalyst. It is proposed that CO oxidation at low temperatures proceeds mainly *via* the reaction between the adsorbed CO on Pd sites and the lattice oxygen of surface CeO₂ at the Pd-Ce interface⁵⁴. The smaller PdO species on the surface of PdO/CPZ catalyst implies more sites for CO chemisorption and an increase in the amount of interfacial Pd-O-Ce sites, which are considered to promote the activities of the catalysts for CO oxidation.

Moreover, the penetration of Zr⁴⁺ cations into the CeO₂ lattice increases the oxygen vacancy concentration from 1.4 of the PdO/CP catalyst to 1.7 of the PdO/CPZ catalyst, as evidenced by Raman spectroscopy (Fig.3). It is believed that oxygen vacancies in CeO₂ or CeO₂ related material play an important role for the catalysts in CO oxidation. The increasing of oxygen vacancy concentration suggests easier activation of oxygen in the samples. The activation of oxygen is usually related to the reducibility of the support, especially when reducible oxides such as CeO₂ are used as the support. The H₂-TPR results clearly show that the redox properties of the PdO/CPZ and CPZ catalysts are enhanced due to the Zr addition in the catalysts. Owing to the presence of oxygen vacancies, CeO₂-based solid solution could serve as an oxygen supplier in the formation of superoxide species (O²⁻) by gas-phase oxygen reacts with oxygen vacancies on its surface or promote lattice oxygen migration and direct involvement in CO oxidation^{55,56}. Thus, the formation of oxygen vacancies in the sample promotes the activation of oxygen species on the catalyst surface, which facilitates the catalysts for CO oxidation.

4.3 Effect of Zr addition in the catalysts for CH₄ oxidation

From the XRF results (Table S1 (Supportion Information)), it can be concluded that the penetration of Zr⁴⁺ cations into the CeO₂ lattice results in the reducing of Pdⁿ⁺ cations in the CPZ solid solution and the increasing of PdO species on the surface of the PdO/CPZ catalyst. The activities of the catalysts for CH₄ oxidation follows the order of CP > PdO/CP, CPZ > PdO/CPZ (Fig.5), implying that the surface PdO species are less active than the Pdⁿ⁺ cations in the CP or CPZ solid solution and the latter contributes

more to the reaction than the surface PdO species. This also indicates that the PdO species is not the active phases for CH₄ oxidation. The suppressed activity of the PdO/CP and PdO/CPZ catalysts could be related to the overlap of PdO species on the surface of catalysts, which weaken the effect of the Pdⁿ⁺ cations in the CP or CPZ solid solution and consequently causes a decline in the activity. Mayernick and Janik⁵⁷ reported that CH₄ molecules could be more easily activated on the Pdⁿ⁺ cations in CeO₂ matrix than that on the PdO species, which implied Pdⁿ⁺ cations contribute to the significant activity of the catalysts for CH₄ oxidation. The similar conclusion is consistent with previous literature reports that the activity of the PdO_x/Al₂O₃ catalyst is related to the Pd/PdO_x ratio and the increasing of PdO sites inhibit the CH₄ oxidation activity of the catalyst⁵⁸.

After the acid treatment, the activity of CP and CPZ catalysts increased obviously. This is because the surface PdO species is removed and the Pdⁿ⁺ cations exposed on the surface of the CP and CPZ solid solution and thus react with CH₄ molecules easily. Li *et al.*⁵⁹ reported that a kind of cationic PdO^{δ+} sites with higher binding energies than PdO are in close vicinity to the oxygen vacancies in the CeO₂ support and might act as the active centers for methane oxidation. Compared with CP catalyst, the CPZ catalyst shows a much lower activity. This suggests that the accumulation of Zr-O-Ce moieties in the CPZ solid solution goes against the CH₄ oxidation. It is reported that the methane activation barrier over the Ce_{1-x}Pd_xO_{2-δ}(111) surface is lower than that over PdO(100) and CeO₂(111), CeO₂(110), CeO₂(100) surfaces, which is due to the enhanced reducibility of CeO₂ surface by the incorporation of Pd ions into the CeO₂ lattice⁶⁰. The penetration of Zr⁴⁺ cations into the Ce_{1-x}Pd_xO_{2-δ} solid solution decreases the amount of Pd-O-Ce moieties and thus suppressed the activity of the catalysts for CH₄ oxidation. In addition, the chemical nature of the Pdⁿ⁺ cations in the Ce_{1-x}Pd_xO_{2-δ} solid solution could also be varied due to the introduction of Zr species and the interaction between Pdⁿ⁺ and Zr⁴⁺ cations may change the catalytic property of the catalysts. To confirm this, theoretical calculations of CH₄ activation on the CP and the CPZ solid solutions will be carried out in the future.

5 Conclusions

This work investigated the effects of Zr addition in the PdO/CP catalyst for CO and CH₄ oxidation. The PdO/CP and PdO/CPZ catalysts were prepared by a solution combustion method and acid treatment method was used to obtain the CP and CPZ catalysts. The Zr addition in the PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst showed different effects for CO and CH₄ oxidation. The enhanced activity of PdO/CPZ catalyst for CO oxidation could be related to the formation of more and smaller surface PdO species and higher oxygen vacancy concentration in the CPZ solid solution. The Pdⁿ⁺ cations in the CP solid solution were believed to be the active sites for CH₄ oxidation. The penetration of Zr⁴⁺ cations into the CeO₂ lattice decreased the amount of Pdⁿ⁺ cations in the CPZ solid solution and thus suppressed the activity of the catalysts for CH₄ oxidation.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

References

- (1) Trovarelli, A.; de Leitenburg, C.; Boaro, M.; Dolcetti, G. *Catal. Today* **1999**, *50*, 353. doi: 10.1016/S0920-5861(98)00515-X
- (2) Sun, C. W.; Xie, Z.; Xia, C. R.; Li, H.; Chen, L. Q. *Electrochem. Commun.* **2006**, *8*, 833. doi: 10.1016/j.elecom.2006.03.018
- (3) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345. doi: 10.1038/35104620
- (4) Padeste, C.; Cant, N.; Trimm, D. *Catal. Lett.* **1993**, *18*, 305. doi: 10.1007/BF00769451
- (5) Teschner, D.; Wootsch, A.; Pozdnyakova-Tellinger, O.; Kröhnert, J.; Vass, E. M.; Hävecker, M.; Zafeiratos, S.; Schnörcha, P.; Jentofta, P. C.; Knop-Gericke, A.; Schlögl, R. *J. Catal.* **2007**, *249*, 318. doi: 10.1016/j.jcat.2007.05.010
- (6) Picasso, G.; Gutiérrez, A.; Pina, M. P.; Herguido, J. *Chem. Eng. J.* **2007**, *126*, 119. doi: 10.1016/j.cej.2006.09.005
- (7) Rocchini, E.; Trovarelli, A.; Llorca, J.; Graham, G. W.; Weber, W. H.; Maciejewski, M.; Baiker, A. *J. Catal.* **2000**, *194*, 461. doi: 10.1006/jcat.2000.2954
- (8) Kašpar, J.; Fornasiero, P.; Graziani, M. *Catal. Today* **1999**, *50*, 285. doi: 10.1016/S0920-5861(98)00510-0
- (9) Zhang, T. Y.; Wang, S. P.; Yu, Y.; Su, Y.; Guo, X. Z.; Wang, S. R.; Zhang, S. M.; Wu, S. H. *Catal. Commun.* **2008**, *9*, 1259. doi: 10.1016/j.catcom.2007.11.013
- (10) Xiao, G. L.; Li, S.; Li, H.; Chen, L. Q. *Micropor. Mesopor. Mat.* **2009**, *120*, 426. doi: 10.1016/j.micromeso.2008.12.015
- (11) Song, Z. X.; Liu, W.; Nishiguchi, H.; Takami, A.; Nagaoka, K.; Takita, Y. *Appl. Catal. A* **2007**, *329*, 86. doi: 10.1016/j.apcata.2007.06.023
- (12) Reddy, B. M.; Bharali, P.; Saikia, P.; Khan, A.; Lorient, S.; Muhler, M.; Grünert, W. J. *Phys. Chem. C* **2007**, *111*, 1878. doi: 10.1021/jp068531i
- (13) Martínez-Arias, A.; Fernández-García, M.; Hungria, A. B.; Iglesias-Juez, A.; Gálvez, O.; Anderson, J. A.; Conesa, J. C.; Soria, J.; Munuera, G. *J. Catal.* **2003**, *214*, 261. doi: 10.1016/S0021-9517(02)00084-2
- (14) Laguna, O. H.; Centeno, M. A.; Romero-Sarria, F.; Odriozola, J. A. *Catal. Today* **2011**, *172*, 118. doi: 10.1016/j.cattod.2011.02.015
- (15) Jia, A. P.; Hu, G. S.; Meng, L.; Xie, Y. L.; Lu, J. Q.; Luo, M. F. *J. Catal.* **2012**, *289*, 199. doi: 10.1016/j.jcat.2012.02.010
- (16) Dutta, G.; Gupta, A.; Waghmare, U.; Hegde, M. S. *J. Chem. Sci.* **2011**, *123*, 509. doi: 10.1007/s12039-011-0089-0
- (17) Zhang, G.; Zhao, Z.; Liu, J.; Jiang, G.; Duan, A.; Zheng, J.; Chen, S.; Zhou, R. *Chem. Commun.* **2010**, *46*, 457. doi: 10.1039/B915027G
- (18) Scurtu, M.; Mihaiu, S.; Caldararu, M.; Zaharescu, M. *React. Kinet. Mech. Catal.* **2012**, *105*, 135. doi: 10.1007/s11144-011-0394-0
- (19) Jin, L. Y.; Lu, J. Q.; Liu, X. S.; Qian, K.; Luo, M. F. *Catal. Lett.* **2009**, *128*, 379. doi: 10.1007/s10562-008-9760-6
- (20) Trovarelli, A. *Catal. Rev.* **1996**, *38*, 439. doi: 10.1080/01614949608006464
- (21) Boaro, M.; de Leitenburg, C.; Dolcetti, G.; Trovarelli, A. *J. Catal.* **2000**, *193*, 338. doi: 10.1006/jcat.2000.2887
- (22) Bozo, C.; Guilhaume, N.; Garbowski, E.; Primet, M. *Catal. Today* **2000**, *59*, 33. doi: 10.1016/S0920-5861(00)00270-4
- (23) Zhou, G.; Shah, P. R.; Kim, T.; Fornasiero, P.; Gorte, R. J. *Catal. Today* **2007**, *123*, 86. doi: 10.1016/j.cattod.2007.01.013
- (24) Christou, S. Y.; García-Rodríguez, S.; Fierro, J. L. G.; Efstathiou, A. M. *Appl. Catal. B* **2012**, *111–112*, 233. doi: 10.1016/j.apcatb.2011.10.004
- (25) Specchia, S.; Conti, F.; Specchia, V. *Ind. Eng. Chem. Res.* **2010**, *49*, 11101. doi: 10.1021/ie100532x
- (26) Kim, Y. T.; You, S. J.; Park, E. D. *Int. J. Hydrog. Energy* **2012**, *37*, 1465. doi: 10.1016/j.ijhydene.2011.10.014
- (27) Ciuparu, D.; Lyubovsky, M. R.; Altman, E.; Pfeifferle, L. D.; Datye, A. *Catal. Rev.* **2002**, *44*, 593. doi: 10.1081/CR-120015482
- (28) Gélin, P.; Primet, M. *Appl. Catal. B* **2002**, *39*, 1. doi: 10.1016/S0926-3373(02)00076-0
- (29) Boronin, A. I.; Slavinskaya, E. M.; Danilova, I. G.; Gulyaev, R. V.; Amosov, Y. I.; Kuznetsov, P. A.; Polukhina, I. A.; Koscheev, S. V.; Zaikovskii, V. I.; Noskov, A. S. *Catal. Today* **2009**, *144*, 201. doi: 10.1016/j.cattod.2009.01.035
- (30) Gulyaev, R. V.; Stadnichenko, A. I.; Slavinskaya, E. M.; Ivanova, A. S.; Koscheev, S. V.; Boronin, A. I. *Appl. Catal. A* **2012**, *439*, 41. doi: 10.1016/j.apcata.2012.06.045
- (31) Mayernick, A. D.; Janik, M. J. *J. Phys. Chem. C* **2008**, *112*, 14955. doi: 10.1021/jp805134s
- (32) Baidya, T.; Marimuthu, A.; Hegde, M. S.; Ravishankar, N.; Madras, G. *J. Phys. Chem. C* **2006**, *111*, 830. doi: 10.1021/jp064565e
- (33) Singh, P.; Hegde, M. S. *Dalton Trans.* **2010**, *39*, 10768. doi: 10.1039/C0DT00480D
- (34) Priolkar, K. R.; Bera, P.; Sarode, P. R.; Hegde, M. S.; Emura, S.; Kumashiro, R.; Lalla, N. P. *Chem. Mater.* **2002**, *14*, 2120. doi: 10.1021/cm0103895
- (35) Bera, P.; Patil, K. C.; Jayaram, V.; Subbanna, G. N.; Hegde, M. S. *J. Catal.* **2000**, *196*, 293. doi: 10.1006/jcat.2000.3048
- (36) Zhou, R.; Zhang, X.; Lu, J.; Hu, G.; Luo, M. *Chem. Res. Chin. Univ.* **2015**, *2*, 288. doi: 10.1007/s40242-015-4326-9
- (37) Jin, J.; Li, C.; Tsang, C. W.; Xu, B.; Liang, C. *RSC Adv.* **2015**, *124*, 102147. doi: 10.1039/C5RA13223A
- (38) Yang, X.; Yang, L.; Lin, S.; Zhou, R. *J. Hazard. Mater.* **2015**, *285*, 182. doi: 10.1016/j.jhazmat.2014.10.062
- (39) Hegde, M. S.; Madras, G.; Patil, K. C. *Accounts Chem. Res.* **2009**, *42*, 704. doi: 10.1021/ar800209s
- (40) Gucci, L.; Beck, A.; Horvath, A.; Koppány, Z.; Stefler, G.; Frey, K.; Sajó, I.; Geszti, O.; Bazin, D.; Lynch, J. J. *Mol. Catal. A-*

- Chem.* **2003**, 204, 545. doi: 10.1016/S1381-1169(03)00337-6
- (41) Cao, H.; Song, W.; Gong, M.; Wang, J.; Yan, S.; Liu, Z.; Chen, Y. *J. Nat. Gas Chem.* **2009**, 18, 83. doi: 10.1016/S1003-9953(08)60088-2
- (42) Ma, L.; Luo, M. F.; Han, L. F.; Chen, S. Y. *React. Kinet. Catal. L* **2000**, 70, 357. doi: 10.1023/A:1010313605332
- (43) Fernández-García, M.; Martínez-Arias, A.; Salamanca, L. N.; Coronado, J. M.; Anderson, J. A.; Conesa, J. C.; Soria, J. *J. Catal.* **1999**, 187, 474. doi: 10.1006/jcat.1999.2624
- (44) Chen, L.; Wang, S.; Chen, C.; Zhang, N. *Transit. Metal Chem.* **2011**, 36, 387. doi: 10.1007/s11243-011-9481-3
- (45) Deshpande, S.; Patil, S.; Kuchibhatla, S. V.; Seal, S. *Appl. Phys. Lett.* **2005**, 87, 133113. doi: 10.1063/1.2061873
- (46) Zhang, F.; Chan, S. W.; Spanier, J. E.; Apak, E.; Jin, Q.; Robinson, R. D.; Herman, I. P. *Appl. Phys. Lett.* **2002**, 80, 127. doi: 10.1063/1.1430502
- (47) Spanier, J. E.; Robinson, R. D.; Zhang, F.; Chan, S. W.; Herman, I. P. *Phys. Rev. B* **2001**, 64, 245407. doi: 10.1103/PhysRevB.64.245407
- (48) Weber, W. H.; Hass, K. C.; McBride, J. R. *Phys. Rev. B* **1993**, 48, 178. doi: 10.1103/PhysRevB.48.178
- (49) McBride, J. R.; Hass, K. C.; Weber, W. H. *Phys. Rev. B* **1991**, 44, 5016. doi: 10.1103/PhysRevB.44.5016
- (50) Su, S. C.; Carstens, J. N.; Bell, A. T. *J. Catal.* **1998**, 176, 125. doi: 10.1006/jcat.1998.2028
- (51) Pu, Z. Y.; Lu, J. Q.; Luo, M. F.; Xie, Y. L. *J. Phys. Chem. C* **2007**, 111, 18695. doi: 10.1021/jp0759776
- (52) Bensalem, A.; Muller, J. C.; Tessier, D.; Bozon-Verduraz, F. *J. Chem. Soc. Faraday Trans.* **1996**, 92, 3233. doi: 10.1039/FT9969203233
- (53) Meng, L.; Jia, A. P.; Lu, J. Q.; Luo, L. F.; Huang, W. X.; Luo, M. F. *J. Phys. Chem. C* **2011**, 115, 19789. doi: 10.1021/jp2056688
- (54) Wang, B.; Weng, D.; Wu, X.; Ran, R. *Appl. Surf. Sci.* **2011**, 257, 3878. doi: 10.1016/j.apsusc.2010.11.083
- (55) Sedmak, G.; Hočevár, S.; Levec, J. *J. Catal.* **2004**, 222, 87. doi: 10.1016/j.jcat.2003.10.006
- (56) Li, C.; Domen, K.; Maruya, K. I.; Onishi, T. *J. Catal.* **1990**, 123, 436. doi: 10.1016/0021-9517(90)90140-F
- (57) Mayernick, A. D.; Janik, M. J. *J. Catal.* **2011**, 278, 16. doi: 10.1016/j.jcat.2010.11.006
- (58) Kinnunen, N. M.; Hirvi, J. T.; Venäläinen, T.; Suvanto, M.; Pakkanen, T. A. *Appl. Catal. A* **2011**, 397, 54. doi: 10.1016/j.apcata.2011.02.013
- (59) Xiao, L. H.; Sun, K. P.; Xu, X. L.; Li, X. N. *Catal. Commun.* **2005**, 6, 796. doi: 10.1016/j.catcom.2005.07.015
- (60) Colussi, S.; Gayen, A.; Camellone, M. F.; Boaro, M.; Llorca, J.; Fabris, S.; Trovarelli, A. *Angew. Chem. Int. Edit.* **2009**, 121, 8481. doi: 10.1002/anie.200903581

Zr 掺杂对 $\text{PdO}/\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$ 催化剂 CO 和 CH_4 催化氧化的影响

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Effects of Zr Addition on CO and CH_4 Catalytic Oxidation over $\text{PdO}/\text{Ce}_{1-x}\text{Pd}_x\text{O}_{2-\delta}$ Catalyst

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Table S1 Pd contents, difference in value of Pd contents in catalysts

Catalyst	Pd Content (w/%) ^a	ΔC_{Pd} (w/%) ^b
PdO/CP	1.70	0.20 ^c
CP	1.50	
PdO/CPZ	1.65	0.28 ^d
CPZ	1.37	

^a determined by XRF technique; ^b difference in value of Pd contents in PdO/CP and CP catalysts, PdO/CPZ and CPZ catalysts; ^c $\Delta C_{\text{Pd}} = 1.70 - 1.50 = 0.20$ (wt. %)

^d $\Delta C_{\text{Pd}} = 1.65 - 1.37 = 0.28$ (wt. %)

Part I The calculation of TOF of PdO species on the surface of PdO/CP and PdO/CPZ catalysts for CO oxidation.

Table S2. Flow rate of CO, CO conversion, amount of CO molecules chemisorbed on the PdO/CP and PdO/CPZ catalysts.

Catalyst	F_{CO} ($\mu\text{mol}\cdot\text{s}^{-1}$) ^a	$X_{\text{CO}}/\%$ ^b	V_{CO} ($\text{mL}\cdot\text{g}^{-1}$) ^c
PdO/CP	0.3	5.5	2.1
PdO/CPZ	0.3	19.4	2.9

^a flow rate of CO; ^b CO conversion at 80 °C; ^c amount of CO chemisorbed on the PdO/CP and PdO/CPZ catalysts.

The amount of PdO/CP and PdO/CPZ catalysts used in CO oxidation is 200 mg.

Assuming the amount of CO molecules chemisorbed on the PdO/CP and PdO/CPZ catalyst are N_1 and N_2 , correspondingly.

$$N_1 = \frac{0.42 \times 10^{-3} \text{ L}}{22.4 \text{ L/mol}} = 1.86 \times 10^{-5} \text{ mol} \quad N_2 = \frac{0.58 \times 10^{-3} \text{ L}}{22.4 \text{ L/mol}} = 2.59 \times 10^{-5} \text{ mol}$$

Assuming the TOF of PdO on the surface of PdO/CP for CO oxidation is

$\text{TOF}_{\text{PdO-1}}$, the TOF of PdO on the surface of PdO/CPZ for CO oxidation is $\text{TOF}_{\text{PdO-2}}$.

$$\text{TOF}_{\text{PdO-1}} = \frac{F_{\text{CO}} \times X_{\text{CO}}}{N_1} = \frac{0.3 \times 10^{-6} \text{ mol/s} \times 5.5\%}{1.86 \times 10^{-5} \text{ mol}} = 0.09 \times 10^{-2} (\text{s}^{-1})$$

$$\text{TOF}_{\text{PdO-2}} = \frac{F_{\text{CO}} \times X_{\text{CO}}}{N_2} = \frac{0.3 \times 10^{-6} \text{ mol/s} \times 19.4\%}{2.59 \times 10^{-5} \text{ mol}} = 0.22 \times 10^{-2} (\text{s}^{-1})$$

Part II The calculation of TOF of Pd^{n+} cations in the CP and CPZ catalysts for CH_4 oxidation.

Table S3 Flow rate of CH_4 , CH_4 conversion, crystal size and cell parameter of CeO_2 ,
Pd content in the CP and CPZ catalysts.

Catalyst	F_{CH_4} ($\mu\text{mol/s}$) ^a	X_{CH_4} (%) ^b	Crystal size of CeO_2 (nm)	Cell parameter of CeO_2 (nm)	Pd Content (wt. %) ^c
CP	0.15	15.2	18.3	0.5407	1.50
CPZ	0.15	10.7	12.9	0.5405	1.37

^a Flow rate of CH_4 in $\mu\text{mol}\cdot\text{s}^{-1}$; ^b CH_4 conversion at 350 °C; ^c Pd content in CP or CPZ solid solution

Scheme S1 Cube and Crystal particle and unit cell of CeO_2 , and ball-and-stick
7model.

Picture S1 Crystal particle of CeO_2 .

Picture S2 One side (top side) of a CeO_2 cube (denoted as side a).

Picture S3 Ball-and-stick model of one side of a CeO_2 cube.

Picture S4 Unit cell of CeO_2 (denoted as cube abc).

Picture S5 Ball-and-stick model of a unit cell of CeO₂.

In a CeO₂ crystal particle, there are three kinds of unit cell as showed in scheme S2. The yellow unit cell in the central exposed only one side (top side), the green unit cell on the edge exposed two sides (top and right sides), and the pink unit cell in the corner exposed three sides (top, front and right sides).

Scheme S2 Unit cell of CeO₂ expose different number of side.

For CP catalyst:

CeO₂ is face-centered cubic structure and a crystal particle contained many unit cell of CeO₂. For CP solid solution, the crystal size of CeO₂ is 18.3 nm, and the cell parameter of CeO₂ is 0.5407 nm. Assuming the number of unit cell in a CeO₂ crystal particle is N_1 ,

$$N_1 = \left(\frac{18.3}{0.5407} \right)^3 = 33.8^3 \approx 34^3 = 39304$$

The number of unit cell of CeO₂ exposed one side is n_{11} , $n_{11} = (34 - 2)^2 \times 6 = 6144$

The number of unit cell of CeO₂ exposed two sides is n_{12} ,

$$n_{12} = (34 - 2) \times 4 \times 2 + 4 \times (34 - 2) = 384$$

The number of unit cell of CeO₂ exposed three sides is n_{13} , $n_{13} = 8$

The number of unit cell of CeO₂ exposed zero side is n_{10} ,

$$n_{10} = 39304 - 6144 - 384 - 8 = 32768$$

The number of sides of unit cell exposed on the surface of a CeO₂ crystal particle

is S_{11} , and the number of total sides of unit cell in a CeO_2 crystal particle is S_{12} .

$$S_{11} = n_{11} \times 1 + n_{12} \times 2 + n_{13} \times 3 = 6144 \times 1 + 384 \times 2 + 8 \times 3 = 6936$$

$$S_{12} = (34 \times 34 \times 34 + 34 \times 34) \times 3 = 121320$$

The percentage of the exposed sides in the total sides in a CeO_2 crystal particle R_1 ,

$$R_1 = \frac{S_{11}}{S_{12}} \times 100\% = \frac{6936}{121320} \times 100\% = 5.71\%$$

The content of Pd in CP solid solution $K_1 = \frac{0.2 \text{ g} \times 1.5\%}{106.4 \text{ g/mol}} = 2.82 \times 10^{-5} \text{ mol}$

Assuming the Pd^{n+} cations dispersed in CP solid solution uniformly. In fact, only the Pd^{n+} cations exposed on the surface of CeO_2 crystal particle contributed to the CH_4 oxidation. It should be noted that a CeO_2 crystal particle is selected as object of study in the calculation of R_1 , and this value is also applicable to the whole CP solid solution.

$$\text{TOF}_{\text{Pd}^{n+}} = \frac{F_{\text{CH}_4} \times X_{\text{CH}_4}}{K_1 \times R_1} = \frac{1.488 \times 10^{-7} \text{ mol/s} \times 15.2\%}{2.82 \times 10^{-5} \text{ mol} \times 5.71\%} = 0.014 \text{ s}^{-1}$$

For CPZ catalyst:

The crystal size of CeO_2 is 12.9 nm, and the cell parameter of CeO_2 0.5405 nm.

Assuming the number of unit cell in a CeO_2 crystal particle is N_2 ,

$$N_2 = \left(\frac{12.9}{0.5405}\right)^3 \approx 24^3 = 13824$$

The number of unit cell of CeO_2 exposed one side is n_{21} , $n_{21} = (24 - 2)^2 \times 6 = 2904$

The number of unit cell of CeO_2 exposed two sides is n_{22} ,

$$n_{22} = (24 - 2) \times 4 \times 2 + 4 \times (24 - 2) = 264$$

The number of unit cell of CeO_2 exposed three sides is n_{23} , $n_{23} = 8$,

The number of unit cell of CeO_2 exposed zero side is n_{20} ,

$$n_{20} = 13824 - 2904 - 264 - 8 = 10648$$

The number of sides of unit cell exposed on the surface of a CeO₂ crystal particle is S_{21} , and the number of total sides of unit cell in a CeO₂ crystal particle is S_{22} .

$$S_{21} = n_{21} \times 1 + n_{22} \times 2 + n_{23} \times 3 = 2904 \times 1 + 264 \times 2 + 8 \times 3 = 3456$$

$$S_{22} = (24 \times 24 \times 24 + 24 \times 24) \times 3 = 43200$$

The percentage of the exposed sides in the total sides in a CeO₂ crystal particle R_2 ,

$$R_2 = \frac{S_{21}}{S_{22}} \times 100\% = \frac{3456}{43200} \times 100\% = 8\%$$

The content of Pd in CPZ solid solution $K_2 = \frac{0.2 \text{ g} \times 1.37\%}{106.4 \text{ g/mol}} = 2.58 \times 10^{-5} \text{ mol}$

Assuming the Pdⁿ⁺ cations dispersed in CPZ solid solution uniformly. In fact, only the Pdⁿ⁺ cations exposed on the surface of CeO₂ crystal particle contributed to the CH₄ oxidation. It must be noted that a CeO₂ crystal particle is selected as object of study in the calculation of R_2 , and this value is also applicable to the whole CPZ solid solution.

$$\text{TOF}_{\text{Pd}^{n+}} = \frac{F_{\text{CH}_4} \times X_{\text{CH}_4}}{K_2 \times R_2} = \frac{1.488 \times 10^{-7} \text{ mol/s} \times 10.7\%}{2.58 \times 10^{-5} \text{ mol} \times 8\%} = 0.008 \text{ s}^{-1}$$