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Introduction

Monolithic catalysts are attractive replacements for conventional carriers in heterogeneous gas–solid phase catalytic reactions.^{1,2} Various gas-phase reactions in industrial applications such as exhaust gases elimination and VOCs catalytic combustion facilitate the development such as the use of the cordierite monolithic structure. High mechanical strength, low thermal expansion coefficient, and low-pressure drop are all characteristics of monolith catalysts.³ These properties are particularly suitable for highly exothermic process such as methane combustion reaction ($\Delta H = -802$ kJ mol⁻¹). At large mass flow rate of air and fuel, monolithic honeycomb structure is a better option for seeking thermal stable catalysts to withstand decomposition.⁴ Washcoats of pre-coated oxides are necessary for cordierite monoliths, which serves as supports for conventional catalysts.

Methane emission from coal mine is known as one of the major source of greenhouse gas.^{5,6} Catalytic combustion of methane has been considered as an alternative to conventional

Oxygen lean conditions Jianhui Jin,^a Chuang Li,^a Chi-Wing Tsang,^b Bin Xu^b and Changhai Liang^{*a} Pd-based monolithic catalysts were prepared using cordierites as supports and used as combustion

Pd-based monolithic catalysts were prepared using condientes as supports and used as combustion catalysts for methane. The catalytic activity was further promoted by Ce–Zr oxides coatings. Oxides with different Ce/Zr ratios were synthesized *via* urea co-precipitation method and fully characterized. Catalytic performance of the monoliths was evaluated by oxygen-lean methane combustion through light-off experiments. Steep conversion curves were observed with oxygen completely depleted below 350 °C over all catalysts. Pd supported on ZrO₂ ignited the reaction at the lowest temperature while similar activities for total oxygen conversion were observed for Zr-rich monoliths. Zr-embedded oxides promoted the activity on oxygen consumption due to the interaction between Zr and Pd at the interface, dispersing and stabilizing Pd particles on the catalyst surface. The addition of Ce further promoted the stability of the catalysts. Compared with Pd/Zr, Pd/Ce1Zr2 showed little deactivation after three successive light-offs and maintained stability after 500 h time-on-stream test. Core/shell Pd particles model was proposed for the activity. Small Pd metal particles on the surface serve as an activation site for methane whereas wrapped PdO in the core stabilized by the Ce–Zr oxides acts as oxygen donor. The extent of reduction of Pd has significant effect on activity in the reaction conditions. Other impacting factors such as different oxygen concentrations and space velocities were also assessed to investigate the extent of the influence on methane catalytic combustion.

Catalytic combustion of methane over Pd/Ce–Zr

oxides washcoated monolithic catalysts under

thermal combustion for total oxidation of methane because heat and/or energy at lower temperature can be produced without NO_x generation. Many catalysts, such as supported noble metals⁷ and composite oxides composed of transition metal oxides (Cr, Mn, Fe, Co, Ni, Cu, etc.),8 perovskites9 and hexaaluminates10 have been employed for methane combustion. Pd-based catalysts are known to be the most efficient catalysts for methane combustion as it is a relatively non-expensive precious metal and could perform better under certain operating conditions.6 However, considering their scarcities, much effort has been made to structurally modify the precious metal containing catalysts, aiming at reducing their amount of usages while improving both catalytic and stability performances.11-13 Catalyst supports with different properties also have significant impacts on the activity.14 Owing to the excellent ability to store and release oxygen molecules (OSC, Oxygen Storage Capacity) and improve the noble metals dispersion,15 ceria are widely used as promoter for combustion reactions of various types. Ceria modified with Zr and many other oxides have been explored to enhance the redox properties and stabilities of supports, aiming to achieve better catalytic abilities.¹⁶ Among them, Ce_{1-r}Zr_rO₂ was representative and widely recognized as one of the excellent catalyst supports.17

The redox nature of the reacting gas and pretreatments of the catalysts both affect the crystallite size, the dispersion and



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the oxidation state of Pd.18 Conventional catalytic combustion of methane takes place under oxygen-rich environment,5 the presence of oxidized palladium species in the catalysts is considered to be the active component during catalytic oxidation.^{19,20} The research on oxygen-lean methane combustion could have important implication such as the application in coal mine methane de-oxygenation processes. However, only a few studies were reported under oxygen-lean condition in which methane concentration is much higher than oxygen concentration stoichiometrically required for complete methane combustion to water and carbon dioxide. Since many side reactions such as partial oxidation and reforming may occur, the nature of the active oxygen species, palladium oxidation state and the combustion mechanism may differ significantly from that of the oxygen-rich conditions. Catalysts developed currently may not be suitable under such a reducing atmosphere. Traditional supported noble metal catalyst, especially the Pd/Al_2O_3 , is active catalyst for low temperature methane combustion under high oxygen/fuel ratio environment. However, for a controlled process at low oxygen/fuel ratio, Pd/Al₂O₃ based catalyst fails to maintain the PdO/Pd ratio due to a phenomenon called the periodic PdO/Pd ratio change (oscillatory behavior) occurs.21 A better catalyst is therefore in need to slow down catalyst decomposition, inhibit carbon deposition and metal sintering under this condition. Providing that Pd supported on Ce-Zr based materials exhibit excellent activities on methane combustion, especially in the field of automobile exhaust elimination serving as three-way converter, similar catalysts could be explored to investigate the activity in oxygenlean condition.

The purpose of this work is to obtain a monolith catalyst formulation that are stable and exhibit high activity for the trace oxygen removal in methane combustion reaction. First, a series of Ce–Zr oxides as coatings was synthesized by co-precipitation method. Pd-based monolithic catalysts with cordierite as support can then be prepared by impregnation on the surface of Ce–Zr oxides. The influence of Ce/Zr ratio, oxygen concentration, gaseous hourly space velocity (GHSV) on the reaction were investigated, together with stability tests of light-offs and timeon-stream experiments to provide a thorough investigation into the active sites and the promoting effects of Ce–Zr oxides of this new type of catalyst.

Experimental

Materials preparation

Ce–Zr mixed oxides were synthesized by co-precipitation method. Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·5H₂O with specific ratio were dissolved in water sequentially. Urea was then added to the mixture (urea : metal = 10 : 1) and the reaction mixture was slowly heated up to 96 °C under stirring and subsequently the reaction was maintained for 24 h at this temperature. The precipitates were then filtered, washed with cold deionized water, dried at 120 °C for 12 h and finally calcined at 550 °C for 4 h. The final oxides were denoted as CexZry, where *x* and *y* correspond to the molar ratios. The oxides were ball-milled in 10 wt% HNO₃ solution for 4 h to obtain homogeneous slurry. Honeycomb cordierite (D = 0.9 cm, L = 1.7 cm) was pretreated with 10 wt% HNO₃ to adjust surface structure attachment, then it was dipped into the oxides suspension and the coated cordierite was then blow-dried. To achieve an average loading of 20%, the coating procedure was repeated twice, followed by calcining the coated monolith in muffle at 700 °C for 2 h. Using conventional impregnation method through dipping the monolith into the aqueous solution of palladium nitrate, followed by drying and then calcining in air at 500 °C for 2 h, a brown-colored catalyst complex was obtained with targeted Pd metal loading on the monolith of about 0.3 wt%.

Characterization

The X-ray diffraction (XRD) measurements of oxides were carried out on a Rigaku D/Max-RB diffractometer with a Cu K α radiation a power of 40 kV and 100 mA. Diffraction data was obtained in the 2θ range between 5° and 90° with a step of 0.02° and scan rate of 10° min⁻¹.

Raman spectra of the oxides were recorded using a 325 nm He/Ne laser source on a homemade device at scanning range of $200-1000 \text{ cm}^{-1}$.

The surface area, pore volume, and pore size distribution of the mixed oxides were calculated from nitrogen adsorption– desorption isotherms at 77 K on Quantachrome Autosorb-iQ. Prior to the measurements, all samples were degassed at 250 °C for 8 h. The surface areas were calculated from BET plots.

 $\rm H_2$ -TPR experiments of oxides and Pd impregnated oxides were performed using Quantachrome ChemBET PULSAR. The powders were first purged under He (100 mL min⁻¹) at 300 °C for 30 min and then cooled to room temperature. TPR measurement was carried out in a flow of 10% H₂/Ar at a rate of 10 °C min⁻¹ up to 800 °C.

X-ray photoelectron spectroscopy (XPS, Escalab250, Thermo Corp.) was carried out to investigate the surface compositions of the oxides. The XPS measurements were performed using an X-ray source of Mg K α (1253.6 eV) with a power of 150 W. Ce 3d, Zr 3d, and O 1s lines were monitored. All core-level spectra were corrected by referring the binding energy of the C 1s neutral carbon peak at 284.6 eV.

TEM images of the catalysts were recorded by FEI Tecnai G2 F30 instrument operated at 200 kV. The catalysts were dispersed in ethanol and sonicated. A single drop of sample was placed onto a 200-mesh copper grid coated with an amorphous holey carbon film.

Catalyst evaluation

All the experiments were performed in a reactor tube surrounded by a furnace. The monolith catalyst was centered in the reactor tube with diameter slightly less than the channel's diameter, and two thermocouples was positioned at top and bottom end of the monolith. A K-type thermocouple was centered within the reactor tube to detect and control the reaction temperature. Temperatures at the bottom and top of the catalyst bed were also recorded.

The catalyst was pretreated by reduction of PdO to Pd under hydrogen atmosphere, during which any impurities should be removed. 10% H₂ in Ar with a total flow of 100 mL min⁻¹ was passed through the Pd/CeZr/ceramic monolith bed for 2 h at 400 °C with temperature ramp rate of 4 °C min⁻¹. The reactor was then cooled down to 250 °C under argon.

In the light-off experiments, a feed gas with 50% of CH_4 , balanced with 3% of O_2 and Ar, was introduced to the catalyst bed through mass flow controller with overall flow at 500 mL min⁻¹ and a GHSV of 30 000 h⁻¹. The reactor temperature was raised to the target value starting from 250 °C at rate of 1 °C min⁻¹. Oxygen concentration was analyzed using an online oxygen detector. Online gas chromatograph was used to identify gas components of the product gas at intervals of 10 min. To evaluate the activity for oxygen consumption, oxygen conversion was adopted, which referred to the ratio of the decreased concentration of oxygen to oxygen inlet, since minor change in volume took place during reaction.

For steady-state experiment, the reactor temperature was slowly decreased to 370 °C under argon after reduction. The feed gases were introduced for the combustion reaction with excess methane for the targeted time period. The oxygen levels were recorded by the oxygen detector at intervals of 300 min.

Results and discussion

Catalyst characterization

XRD analysis allows identification of the structures of particles. As shown in Fig. 1, diffraction peaks correspond to ZrO_2 and fluorite cubic phase of CeO_2 (*Fm3m*, JCPDS 34-0394) without significant shifts. The intensities of CeO_2 diffraction peaks decreased gradually with decreasing Ce/Zr ratio, implying gradual change from large to small size of crystalline and poor crystallinity. On the other hand, diffraction peaks of ZrO_2 shift to higher angle, indicating a change of crystalline phases of ZrO_2 (from *Fm3m* 49-1642 to *P4*₂/*nmc* 50-1089), during which metastable tetragonal (t'') emerges in the mixed oxides state.²² No monoclinic ZrO_2 phase was observed. These results indicated that Zr ions partially entered the ceria lattice in the form



Fig. 1 XRD patterns of Ce-Zr oxides with different Ce/Zr ratios.

of solid solution and eventually distorted the crystalline structure.

The BET surface areas for CeO₂, Ce2Zr1, Ce1Zr1, Ce1Zr2 and ZrO_2 were 86, 100, 59, 61 and 90 m² g⁻¹, respectively. The incorporation of ZrO₂ increased the BET surface area at first, but was dropped significantly and exhibited poorer crystallinity with further addition. The surface area increased slightly when the ratio of Ce/Zr decreased below 1, but were lower than the respective pure CeO₂ and ZrO₂, implying the synthesized samples were not simply mechanical mixes of two individual pure oxides. By using co-precipitation method using $Ce(NO_3)_3$ and Zr(NO₃)₄ as precursors and urea as precipitating agent, the presence of heterogeneous mixed oxides in the form of CeO₂ or ZrO2-embeded solid solution were thus confirmed. Surface area of the catalysts was also calculated, and the results were shown in Table 1. After coating and thermal treatment, surface area dropped drastically, especially for ceria. Zirconia helped preventing the incineration of oxides. Compared with reaction results, the surface area was not a dominant factor for catalytic activity.

Raman spectra were illustrated in Fig. 2, and all samples showed two characteristic peaks at 440 cm⁻¹ and 650 cm⁻¹. Peak at 440 cm⁻¹ corresponds to the F_{2g} Raman active mode of the fluorite-like structure. The peak at 640–660 cm⁻¹ indicates the intensity of oxygen defects due to the incorporation of Zr and E_g active mode of tetragonal phase of zirconia, which belongs to tetragonal displacement of some O atoms from their ideal position in the fluorite structure. With the increasing doping of zirconia, the peak shifts to higher wavenumber, which may be due to the crystal phase transfer of ZrO_2 .²³ And the intensity of peaks, so as to the oxygen vacancy increased, and then decreased at Ce1Zr2 due to the drop of Ce amount in oxides. Combined with catalytic results, the defects of oxides caused by doping of zirconia benefitted catalytic activity in comparison with bulk CeO₂.

As shown in Fig. 3, H_2 consumption is attributed to the reduction of surface and bulk CeO₂, since Zr⁴⁺ is an irreducible cation in this temperature range. Pure CeO₂ exhibits two reduction peaks: the first peak centered at around 500 °C corresponds to the reduction of the uppermost layers of Ce⁴⁺; the second peak centered on 800 °C originates from the reduction of the bulk CeO₂.²⁴ The broad reduction peak of CeO₂ and Ce1Zr2 in the temperature range 450–700 °C corresponds to the reduction of surface Ce⁴⁺, while the reduction temperature for bulk CeO₂ is above 800 °C. With further addition of Zr, two dominant reduction peaks instead of one for surface reduction

 Table 1
 Surface area, Pd loading of catalysts and catalytic activity of monoliths promoted by various CeZr coatings for the oxygen-lean methane combustion

Coating	$BET\left(m^2~g^{-1}\right)$	Pd loading	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
CeO ₂	3	0.28	317.3	329.0	330.2
Ce2Zr1	8	0.30	318.9	330.4	331.4
Ce1Zr1	7	0.27	311.2	323.0	324.3
Ce1Zr2	5	0.29	311.6	323.3	324.2
ZrO_2	13	0.28	303.0	322.2	324.7

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Fig. 2 Raman spectra of Ce2Zr1, Ce1Zr1 and Ce1Zr2.

were found. The reduction peaks shifted to lower temperature thus the oxides are much easier to be reduced. For Ce1Zr2, peak belongs to bulk CeO₂ reduction shifted significantly to a lower temperature which is close to the reduction peak of surface Ce^{4+} , forming two shoulder peaks below 700 °C. A possible "shell/core structure" with heterogeneous surface elemental distribution like embedding can be described on the phenomenon of bimodal H₂-TPR profile.²⁵ Combining the information from XRD, BET, Raman and TPR, it can be concluded that the Ce–Zr oxides are a mixture of solid solution and pure Ce or Zr oxides.

Due to the low loading of oxides on cordierites, Pd impregnated oxides was synthesized to evaluate the interaction between Pd and oxides. As shown in Fig. 4, the flat peaks at around 500 °C were assigned to the reduction of surface Ce^{4+} ions, which showed only small difference for the 5 catalysts. Three H₂ consumption peaks at about 100, 150, 230 °C were found for ceria promoted catalysts, while a gentle peak at 150 °C plus a negative peak for hydrogen release were found for Zr doped catalysts. For ceria promoted catalyst, the peak at 100 °C could be assigned to the reduction of surface PdO species, while peaks at 150 and 230 °C could be assigned to the reduction of Pd^{n+} species in $Ce_{1-x}Pd_xO_{2-\delta}$ solid solution structure.²⁶ For Zr doped catalysts, negative peaks at 100 °C was attributed to the decomposition product of Pd hydride formed during H2-TPR,27 indicating the existence of metallic Pd in catalysts. Unlike Pd/CeO₂, peaks at 150 °C were much weaker for catalysts doped with Zr, indicating that Zr weakened the interaction between Pd and ceria, and PdO was much easier to be reduced. With increasing doping of Zr, peaks for hydrogen release shifted to lower temperature region and the intensity increased, and peaks for hydrogen consumption decreased, indicating an increased in Pd/PdO ratio of the catalysts. The doping of Zr in ceria lattice weakened the bond of Ce-O-Pd, making Pd expose to the outer surface of the ceria lattice and keep a moderate interaction between Pd and the ceria.

The elemental composition and chemical valence on the surface of the as-prepared Ce–Zr oxides were detected by XPS to investigate the relationship of activity and coating oxides. As exhibited from Fig. 5, the surface ratio of Ce to Zr are 2.7 and 0.33, which are different from the theoretical value for Ce2Zr1 and Ce1Zr2, revealing that Ce or Zr-rich phases appeared on the surface of each sample, forming a shell/core structure.²⁸

The seemingly complex spectrum of Ce 3d can be decomposed into 10 peaks for analyses, the bands v' and u' are the satellites arising from the Ce $3d_{5/2}$ and Ce $3d_{3/2}$ ionizations of Ce³⁺, indicating the generation of oxygen vacancies.²⁹ The chemical valence of cerium on the surface contains Ce³⁺ and Ce⁴⁺, with the ratio of Ce³⁺/Ce as 0.29 and 0.35 for Ce2Zr1 and Ce1Zr2, respectively. The surface concentration of Ce³⁺ to Ce on the as-prepared oxides was enhanced by increasing the addition of zirconia and thus more oxygen vacancies exist in CeO₂ lattice. O 1s spectra fitted with two peaks, one band located at 529.3–529.6 eV and a peak at the higher BE of 531.1–531.4 eV.



Fig. 3 H_2 -TPR profiles of the oxides prepared with different Ce/Zr ratios.



Fig. 4 H₂-TPR profiles of PdO/oxides with different Ce/Zr ratios.



Fig. 5 XPS spectra of Ce 3d and O 1s for Ce2Zr1 and Ce1Zr2 oxides.

The former is characteristic of lattice oxygen associated with cerium or zirconium and the latter belongs most likely to defective oxide or hydroxyl-like groups. A shift slightly towards higher BE for the lattice oxygen peak of Ce1Zr2 than Ce2Zr1 is coherent with the conversion of part of Ce⁴⁺ into Ce³⁺ species.³⁰

Since the Pd/Ce1Zr and Pd/Zr showed similar ignition performance, TEM images of the two catalysts were shown in Fig. 6. Pd was hard to find in Pd/Ce1Zr2 due to the background of ceria lattice, the low loading of Pd, finely dispersed or interacted with ceria to form Ce–O–Pd.²⁶ In Pd/Zr catalyst, Pd particles were clearly dispersed on Zr with particle sizes among 3–8 nm. Compared with catalytic activities and stability tests below, the main role of ceria is to stabilize Pd.

Oxygen elimination activity

Oxygen conversion was used as the key indicator for assessing catalytic activity using online oxygen detector with detect limit of 0.01%. Since methane combustion took place in such scarce oxygen environment, methane may undergo partial oxidation or reforming. However, due to the enormous concentration gradient between methane and products, it is quite difficult to quantify the outputs precisely through gas chromatography.



Fig. 6 TEM images of Pd/Ce1Zr (a), (c) and Pd/Zr (b), (d)

Using GC to analyze the formed gases, at the early stage of reaction before ignition, no significant hydrogen produced, and indicating methane was completely oxidized. When ignition happened, H_2 appeared, partial oxidation of methane took place due to the lack of oxygen. When oxygen was completely removed, the signal of H_2 increased.

Results of light-off experiments were shown in Fig. 7 and presented in Table 1, where T_{10} , T_{50} and T_{90} of the catalysts correspond to the temperature needed to reach 10, 50 and 90% oxygen conversion, respectively. After catalysts reduction, reactants were introduced at 250 °C at which temperature the catalysts would not have any activity for oxygen consumption. With programmed elevation of temperature, the catalytic activity increased gradually. When the oxygen conversion increased to some level (at about 20%), a subtle increase in activity accompanied with large amount of heat release was observed for all catalysts, and oxygen was completely consumed at below 350 °C. Two aspects contribute to this phenomenon. The first is heat accumulation: during methane oxidation under such flow rate, the monolith cannot radiate its surplus of heat to



Fig. 7 Oxygen conversion *versus* temperature over catalysts with different Ce/Zr ratios.

surroundings efficiently, resulting in the rise of reaction temperature at catalyst surface. The second corresponds to chemical/physical change of the active sites. At the beginning of the reaction, metallic state of Pd dominates. As temperature increases, palladium was re-oxidized progressively by oxygen in the reactants, leading to the formation of Pd/PdO and eventually to PdO. The surface of PdO was then reduced again owing to the reducibility of methane, plus the formation of reaction products such as H₂O, CO₂, etc. The sudden increase in activity took place right at the temperature reported where large PdO particle was reduced under CH₄/N₂.³¹ There may be a correlation between activation energies and surface Pd valances: when the surface was dominated by PdO at low temperature, the activation energy was greater, leading to low conversion at low temperature; less energy barrier emerged with sharp increase in oxygen conversion when metallic Pd was dominant. The final state of palladium strongly depends on the properties of supports. As the addition of Zr increased, the activity of methane combustion decreased first, followed by a further increase at lower Ce/Zr ratio. Pd supported on pure ZrO₂ exhibited the best ignition activity while activity for total conversion was similar when Ce/Zr ratio equals to or below 1. Catalysts supported by Zr-rich oxides were more active than Ce-rich ones in methane combustion under oxygen-lean conditions.

Comparing catalysts supported by different Ce-Zr oxides, Pd maintained at partial +2 states by oxygen contributed from ceria lattice due to the high OSC of ceria, which can be further oxidized by O2 and H2O. On the contrary, Pd supported on zirconia-rich oxides is easier to be reduced under such reducing atmosphere. With the decrease in Ce/Zr ratio, much facile reducibility for zirconia-rich oxides is deduced from H2-TPR. However, oxygen storage capacity decreased with more ZrO₂ in the oxides, causing palladium more prone to be reduced to metallic Pd. Therefore higher metallic Pd ratio in Pd particles is more beneficial for methane combustion in such reaction condition, especially at the ignition period. Unlike methane combustion in air, the redox ability of ceria in the catalyst was not prominent for oxygen elimination in excess methane. The more useful property may be the fixation of Pd by oxygen vacancies which promotes stabilization. However, a relatively low temperature for total oxygen conversion was found with catalysts promoted by Ce-Zr mixed oxides. The properties of supports such as OSC may cause significant effect at the final stage when only scarce amount of oxygen left. Due to the strong interaction between CeO2 and interfacial Pd, partial PdO was sustained in the catalyst and further Pd agglomeration was prevented. It implies that rapid oxygen exchange between the surface and the lattice has significant effect on total oxygen conversion via the maintenance of a desirable PdO/Pd ratio.

Although there is a big difference among the TPR profiles, so as the properties of catalysts. However, the catalytic activity difference was not apparent. All the 5 catalysts showed steep oxygen conversion, which was usually found in homogeneous reactions. However, it was not quite possible since the reaction temperature was not high enough to support homogeneous reactions. A possible explanation is the comparative adsorption between oxygen and methane. The stick coefficient of oxygen is larger than methane at low temperature, and the surface of catalysts are covered by oxygen, inhibiting the adsorption of methane. When the reaction reached the temperature for oxygen desorption, the dissociative adsorption of methane took place. Once the cracking of methane happened, oxygen was consumed immediately by methane radicals, which resulted in the steep oxygen conversion. The little difference between the catalysts lied in the ability of methane activation. Due to the low coverage of oxygen, the ignition temperature was much lower than traditional methane combustion reaction.

Catalysts with different Pd loadings referring to the whole monolith were prepared using Ce1Zr2 as coating. As exhibited in Fig. 8, by increasing the loading of Pd from 0.17 wt% to 0.48 wt%, temperature for total oxygen conversion decreased gradually (from 332.7 °C to 322 °C). And similar activity was observed for Pd loadings with 0.40 and 0.48 wt%. The light-off results suggested that there is an optimum Pd content for the monolith catalysts in methane combustion.³² Furthermore, there was no oxygen consumption when reaction temperature was below 280 °C, regardless of the amount of Pd loading. Oxygen consumption began at temperature close to the CH₄-TPR data on Pd/Al₂O₃ reported by Baylet *et al.*³¹ Since catalyst supported by irreducible ZrO₂ had the lowest ignition temperature, the results implied that metallic Pd may be the active site for the early stage of the reaction.

To understand the role of oxygen in the reaction, different concentrations of oxygen were introduced over the catalyst supported by Ce1Zr2 while keeping methane concentration at 50% and GHSV at 30 000 h⁻¹. The effect of oxygen concentration was illustrated in Fig. 9. Volcano-like activity was observed by increasing oxygen concentration from 2% to 5% taking T_{100} as reference. Oxygen elimination activity increased linearly as oxygen concentration increased from 2% to 4%. However, T_{100} rose when oxygen concentration was further increased to 5%. By increasing oxygen partial pressure, surface Pd is more prone to be oxidized, exposing a thinner layer of active Pd on the surface. For conventional methane combustion, optimum ratio of



Fig. 8 Effects of Pd loadings on light-off activity.



Fig. 9 O_2 concentration effects on the conversion of O_2 over catalyst supported by Ce1Zr2.

PdO/Pd was proposed for methane activation.³³ A similar phenomenon exists in oxygen lean conditions. According to Mars-van Krevelen mechanism,⁵ methane is adsorbed onto the active sites and reacts with lattice oxygen on the surface. The oxygen vacancies are then replenished by gas phase oxygen. With more oxygen replenished, competitive adsorption takes place, and the number of vacancies and metallic Pd decreases, leaving lesser sites for methane adsorptions. Besides, higher oxygen conversion rate occurred when oxygen concentration increases due to the generation of more heat during oxidations, agglomeration of Pd was thus more apt to take place. In all cases, oxygen was totally consumed below 350 °C, indicating that the catalyst can keep its activity in a wide range of oxygen concentration under oxygen-lean conditions.

With reference to the model proposed by Assmann *et al.*³⁴ the processes and the core/shell structure of catalyst were illustrated in Scheme 1. The pre-reduced particles were totally oxidized at the early stage of the reaction. Increasing the temperature under net reducing conditions leaded to a gradual reduction of the outer PdO layer to metallic Pd. The rate of metallic Pd layer formation and its thickness were controlled by



Scheme 1 The core/shell model of Pd particles and the interaction between Pd and coating oxides.

the concentration of oxygen feed. Thus, active metallic Pd sites were exposed to the gas phase. The PdO core was stabilized by its interaction with supporting oxides.

One of the advantages of monoliths is low-pressure drop, so the flow velocities of reactants can be insured to operate at a wide variety. As shown in Fig. 10, space velocities of 10 000, 30 000 and 50 000 h⁻¹ were chosen to investigate the flow rates applicability of the monolithic catalysts over the catalyst promoted by Ce1Zr2. Higher O2 conversion activity was found at relatively high GHSV though having shorter residence times of reactant gases. Besides, a gentle oxygen conversion curve was acquired at lower velocity of 10 000 h^{-1} . The heat generated during reaction was indicated via outlet temperature. There was no difference on outlet temperature among the three flow rates when reaction temperature was below 310 °C with oxygen conversion below 20%. Outlet temperature increases significantly when sharp oxygen conversion occurred, and higher temperature was found at higher velocity. Since methane combustion is exothermic, higher GHSV would generate more heat at the surface of the catalyst.35 The elevated surface temperature accelerated the reaction rates, thus promoting the consumption of oxygen.

Catalyst stability

Stability is one of the key criteria for catalyst assessment, since the sustainability of structure and surface components are essential for catalysts to have long time operation. Two kinds of tests were conducted over the catalyst coated by Ce1Zr2 with reactants of 50% CH₄, 3% O₂ and 47% Ar at GHSV of 30 000 h⁻¹: three cycles of light-off experiments (Fig. 11a) and time-onstream experiment at 370 °C (Fig. 12). After 3 times of lightoff, temperature for total oxygen conversion shifts to 5 °C higher. However, the methane activation temperatures decreased since T_{50} of the second and the third were lower than the first one. The phenomenon reported by Demoulin *et al.* for catalytic combustion of methane over Pd/Al₂O₃ catalyst stated that under reaction conditions of time-on-stream, activity



Fig. 10 Effect of GHSV on O_2 conversion over the catalyst promoted by Ce1Zr2 (inset shows outlet temperature *versus* furnace temperature).





Fig. 11 Stability of the catalyst promoted by (a) Ce1Zr2, (b) Zr through successive light-off experiments.

increased due to the sintering of Pd particles.36 During the initial heating, slight aggregation of the palladium phase occurred owing to the reducing circumstance and hot pots generated by combustion, which seems to be beneficial for the ignition activity. But sharp decreases in activity were found during the second and third heating curves when the oxygen conversion increased to about 80%, and the temperature interval for activity regaining becomes greater. Only after the conversion dropped to a specific low level (about 30%), the activity increased again. Similar but not such severe oscillation phenomenon has been reported in the case of conventional methane combustion.37 Oscillation happened when reaction temperature reached 700-800 °C, which was attributed to the decomposition of PdO. X. Zhang et al. believed oscillation occurs when the surface of the catalyst undergoes cycles of oxidation and reduction, between a highly active oxide state and a less active metal-rich state.³⁸ When the removal of oxygen from the oxide lattice exceeds the rate of replacement through adsorption of oxygen, the oxide will be rapidly reduced to the metal. We speculate the larger margin and lower temperature for oscillation is due to the scarcity of oxygen, which made PdO more prone to be reduced. Zhang et al. studied the oscillatory behavior under various temperatures and methane/oxygen gas ratios, and ascribed the behavior to the failure of efficient transformation between PdO and Pd.39 During several times of temperature elevation and the existence and vanish of oxygen, the valence of palladium on catalyst surface underwent continual change throughout the reaction. The surface PdO particles, especially smaller ones would be easily reduced and aggregated to larger particles through re-dispersion, leaving less active site for methane adsorption. Besides, since larger surface layer of PdO particles were harder to be reduced, they would benefit the initial activity at the early stage of each light-offs. However, larger PdO particles failed to exchange with gas phase oxygen efficiently when oxygen conversion reached some level, resulting in the occurrence of oscillation. Besides, much higher temperature was needed for the dissociation of methane.

Because Pd/Ce1Zr2 and Pd/Zr had better activity for oxygen elimination, successive light-off experiments were also performed on Pd/Zr to compare the stability of catalysts (Fig. 11b). Similar to Pd/Ce1Zr2, oscillations appeared after first ignition. However, oscillation became severe at the third light-off and temperature for total oxygen conversion shifted to higher temperature, which indicates zirconia failed to maintain the stability of catalyst.

Since severe, continuous and ruleless oscillations may happen when oxygen conversion didn't reach 100%, stability test of Pd/Ce1Zr2 after second cycle is attempted to perform at 330 and 350 °C for 12 h. The oxygen conversion maintained 100% for Pd/Ce1Zr2 at 350 °C. When the reaction temperature lowered to 330 °C, gradual deactivation with gentle oscillation appeared, and oxygen conversion dropped to 99% after 12 h test.

To examine the long-time stability for industrial purpose, a fresh catalyst was used. Time-on-stream stability test was conducted under a feed gas with 50 vol% CH_4 , 3 vol% O_2 and balancing Ar at 370 °C with GHSV at 30 000 h⁻¹ and kept for 500 h. Fluctuation of inlet and outlet temperatures was observed during the test, and became greater with prolonged time. During the 500 h stability test, a gradual deactivation exhibited with the conversion of oxygen decreasing from 100% to 98%. Neither sudden deactivation nor severe oscillation was discovered. The catalyst exhibits excellent stability under excess methane with scarce oxygen condition, and Pd particles were well stabilized by Ce–Zr oxides.

Unlike light-off experiments that surface palladium experienced a continuous transition from PdO and Pd, metallic Pd



Fig. 12 Stability test of the catalyst Pd/Ce1Zr2 (a) stability after second cycle of ignition (T = 350 °C and 330 °C), (b) long-time stability for 500 h (T = 370 °C, GHSV = 30 000 h⁻¹).

may be the main form of surface layer under time-on-stream circumstance.³¹ The catalyst is always in the reducing condition since oxygen is totally consumed. No obvious deactivation was discovered, which indicated that the ratio of PdO and Pd was kept constant in the reaction condition and Pd particle size was maintained due to the stabilization by Ce–Zr oxides.

Conclusions

Applying monolithic catalysts of Pd/Ce-Zr, oxygen was eliminated thoroughly under excess methane environment. With relatively low palladium loadings (0.3 wt%), the catalysts showed excellent catalytic activity at low temperature. Complete consumption of oxygen could be reached below 350 °C. Catalysts with appropriate Pd loadings and promoted by Zr-rich oxides exhibit excellent catalytic performance. An optimum Pd/PdO ratio stabilized by CeZr coatings was proposed of importance for methane activation and oxygen elimination. The investigation of operation parameters such as oxygen concentration and GHSV on the activity of catalyst promoted by Ce1Zr2 indicated that the catalyst exhibited good activity over a wide range of oxygen concentrations, and was active even when GHSV reached 50 000 h^{-1} . With similar initial activity, Pd/Ce1Zr2 kept high stability after three successive light-offs, while the activity of Pd/Zr dropped dramatically. The time-onstream experiments further confirmed that the Pd/Ce1Zr2 catalyst had good stability after running for 500 h. The results on the stability of the catalyst and the residual O2% level of the product gas provided insight into the feasibility and optimization of this catalytic combustion process. These findings indicated that the as-prepared monolithic catalysts may be a promising alternative catalytic technology to oxygen removal of coal mine methane and worthy of further exploring for other applications in catalysis.

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