



## The effect of CeO<sub>2</sub> and BaO on Pd catalysts used for lean-burn natural gas vehicles

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### ABSTRACT

Palladium catalysts supported on Al<sub>2</sub>O<sub>3</sub> doped by BaO and/or CeO<sub>2</sub> were prepared by impregnation method. Various techniques, including N<sub>2</sub> adsorption (Brunauer–Emmet–Teller method; BET), X-ray diffraction (XRD), CO-chemisorption, H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) and X-ray photoelectron spectroscopy (XPS), were employed to characterize the effect of BaO and/or CeO<sub>2</sub> on the physicochemical properties of prepared catalysts. Catalytic activities for methane and CO oxidation were evaluated in a gas mixture simulated the exhaust from lean-burn natural gas vehicles (NGVs). The BET results showed that the supports possessed high specific surface area, suitable pore volume and pore size distribution. The activity results indicated that the catalyst modified by CeO<sub>2</sub> showed the best performance for methane and CO removal, and the one modified by both BaO and CeO<sub>2</sub> the worst. CO-chemisorption and H<sub>2</sub>-TPR results indicated that the addition of ceria or barium alone could increase the dispersion of palladium and improve the reducibility of catalysts. The results of XPS showed that BaO increased the electron density around PdO while CeO<sub>2</sub> activated the lattice oxygen and increased the content of oxygen species on the surface of catalysts. When BaO and CeO<sub>2</sub> were added simultaneously, their respective potential effect was restrained by each other resulting in the decrease of catalytic activity.

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### 1. Introduction

With the deterioration of environment and decreasing of oil resources, lean-burn natural gas fuelled vehicles (NGVs) has aroused considerable attention, because of its economy, less CO<sub>2</sub> emission, less NO<sub>x</sub> and particulates in the exhaust compared with gasoline and diesel engines [1–5]. However, there is still high level of unburned methane in the exhaust. Methane is a potent greenhouse gas, which is estimated to have a 20-year global warming potential 35 times that of carbon dioxide at equivalent emission rates [3], so it must be reduced by catalytic converter before emitted into the atmosphere. Methane is the most stable hydrocarbon molecule and is very difficult to be converted, and its conversion needs high temperature and excellent catalysts. However, the temperature of the exhaust from NGVs is low, typically lower than 550 °C. Furthermore, in the exhaust, there are water vapor (about 10–15%), carbon dioxide (10–15%), large excess of oxygen and little SO<sub>2</sub> and NO<sub>x</sub>. These all increase the difficulties of methane conversion and

require the use of specific catalysts with high catalytic activity able to oxidize methane at lower temperatures under strongly lean-burn conditions [6,7].

Many studies have focused on the palladium supported alumina catalysts that are accepted widely as the most active catalysts for methane oxidation under lean conditions. Different additives such as Ce, Ba, La, and Zr have been used to improve the properties of Pd catalysts [8], especially Ba and Ce, which are often used in three-way catalysts. Generally, BaO is used to improve thermal stability of Al<sub>2</sub>O<sub>3</sub> supports and promote catalytic activity for methane combustion at high temperature. CeO<sub>2</sub> has the ability to storage/release oxygen, which is also used to improve the thermal stability of supports, and is beneficial to stabilize active PdO and to increase PdO dispersion by interaction with PdO, thus enhance the catalytic activity [8]. Many researches have been made to investigate the influence of CeO<sub>2</sub> or BaO alone on the activity and thermal stability at temperature as high as 1000 °C for catalytic combustion of methane [9–11]. Liotta and Deganello [12] have investigated Pd catalysts supported on Al<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>–BaO with different cerium contents used for methane combustion. It is concluded that when ceria loading is lower, about 4–8 wt%, the catalyst has the best activity, and with CeO<sub>2</sub> content increasing, the catalytic activity for methane combustion is decreasing. But their conclusion is made on the presence

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of both ceria and barium, and they did not investigate the activity of catalysts supported on  $\text{Al}_2\text{O}_3$  doped with  $\text{CeO}_2$  or  $\text{BaO}$  alone. Klingstedt et al. [13–15] have also investigated the  $\text{CeO}_2$  and  $\text{BaO}$  separately modified catalysts used for NGVs operated under stoichiometric condition. They find that the addition of  $\text{CeO}_2$  or  $\text{BaO}$  can promote catalytic activity for methane conversion, CO oxidation and  $\text{NO}_x$  removal, widen the lambda window, and improve the hydrothermal stability of Pd catalysts. There are very few studies on palladium supported on  $\text{Al}_2\text{O}_3$  doped with  $\text{CeO}_2$  or  $\text{BaO}$  used for the oxidation of methane and CO at low temperature under lean-burn NGVs exhaust condition, and much fewer on the supported catalysts doped with  $\text{CeO}_2$  and  $\text{BaO}$  at the same time.

In this paper, palladium catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$  modified by  $\text{CeO}_2$  and/or  $\text{BaO}$  were prepared. The catalysts were evaluated in a gas mixture simulated the exhaust of lean-burn natural gas vehicles at low temperatures.  $\text{N}_2$ -adsorption method, X-ray diffraction (XRD), CO-chemisorption and catalytic activity testing investigated the influences of the addition of  $\text{CeO}_2$  and  $\text{BaO}$  on the textural, structural and catalytic properties of palladium catalysts.  $\text{H}_2$ -temperature-programmed reduction ( $\text{H}_2$ -TPR) and X-ray photoelectron spectroscopy (XPS) were employed to investigate the interaction between palladium and  $\text{BaO}$  or  $\text{CeO}_2$ .

## 2. Experimental

### 2.1. Support and catalyst preparation

$\text{Al}_2\text{O}_3$ ,  $\text{BaO-Al}_2\text{O}_3$ ,  $\text{CeO}_2\text{-Al}_2\text{O}_3$  and  $\text{BaO-CeO}_2\text{-Al}_2\text{O}_3$  were prepared by co-precipitation method.  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was used as precursor, dissolved in distilled water, then mixed with the solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$  and the mixture of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ba}(\text{NO}_3)_2$  separately. Then the mixed solutions were precipitated by adding excessive mixture solution of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{CO}_3$ . During the titration, pH was kept at 9.5. After co-precipitation process, the precipitates thus obtained were boiled, filtered, washed, dried and then calcined at  $900^\circ\text{C}$  for 4 h. The nominal contents of  $\text{BaO}$  and  $\text{CeO}_2$  were both 4 wt% for modified supports.

The Pd catalysts were prepared by impregnation of modified supports with  $\text{Pd}(\text{NO}_3)_2$  solutions. The Pd content is 1.4 wt%. Then the catalysts were dried at  $120^\circ\text{C}$  overnight, calcined at  $550^\circ\text{C}$  for 2 h. Monolithic catalysts were obtained as follows: the prepared powder catalysts were ball-milled with proper amount deionized water to obtain homogeneous slurry, then the resulting slurry were spread onto a honeycomb cordierite ( $2.5\text{ cm}^3$ , Corning, China). Excess slurry was blown off using compressed air. The obtained Pd loading was about 2.5 g/L and the washcoat loading was 180 g/L. The coated catalysts were dried overnight at  $120^\circ\text{C}$ , calcined at  $550^\circ\text{C}$  for 2 h. They were labeled as PdAl, PdBaAl, PdCeAl, and PdBaCeAl.

### 2.2. Catalytic activity measurements

Catalytic activity test was carried out on monolithic samples in a multiple fixed-bed continuous flow micro-reactor by passing a gas mixture simulated the exhaust emissions from lean-burn natural gas vehicles. The test was performed from 240 to  $500^\circ\text{C}$  with an interval of  $20^\circ\text{C}$ , and repeated tests were carried out until the conversion was constant. The simulated exhaust contained  $\text{CH}_4$  0.063 vol.%, CO 0.40 vol.%, NO 0.063 vol.%,  $\text{O}_2$  5.0 vol.%, and  $\text{CO}_2$  12.0 vol.%,  $\text{N}_2$  as balance gas. The gas space velocity was  $34000\text{ h}^{-1}$ . The gases were regulated by mass-flow controllers before entering reactor. The concentration of  $\text{CH}_4$  was analyzed by on-line gas chromatography equipped with FID detector, and CO was analyzed online by a five-component

analyzer FGA-4100 (Fofen Analytical Instrument Co. Ltd., China), before and after the simulated gases passing through the reactor.

### 2.3. Support and catalyst characterization

The BET specific surface area and pore size measurements were performed by adsorption/desorption of  $\text{N}_2$  at the liquid nitrogen temperature on a ZXF-06 automatic surface analyzer (Xibei Chemical Institute, China). Before adsorption measurement, the samples were degassed in vacuum for 2 h at  $400^\circ\text{C}$ .

The crystal structures of the samples were determined by a power X-ray diffraction on a DX-1000 diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406\text{ nm}$ ) and operating at 40 kV and 25 mA. The XRD data were recorded for  $2\theta$  values between  $10^\circ$  and  $90^\circ$  with an interval of  $0.03^\circ$ . The scanning way was continuous scanning for PdAl and PdBaCeAl with 1 s count accumulation time per step, and progressive scanning for PdBaAl and PdCeAl with 2 s count accumulation time per step. The crystalline phases were identified by comparison with the reference data from the International Center for Diffraction Data (ICDD).

The metal dispersions and mean particle sizes of palladium on four supports were determined by CO-chemisorption over reduced catalysts. Approximately 300 mg sample was placed in an U-shaped quartz tube. Prior to chemisorption, the catalyst was reduced in a flow of  $\text{H}_2$  (30 ml/min) at  $550^\circ\text{C}$  for 1 h, and then purged with pure  $\text{N}_2$  for 1 h. After cooled down to room temperature, carbon monoxide was pulsed over the reduced catalyst until the thermal conductivity detector (TCD) signal from the pulse was constant. The number of exposed Pd atoms was calculated assuming a chemisorption stoichiometry of  $\text{CO}/\text{Pd} = 1$  and all CO was adsorbed on exposed Pd atoms [16,17], and mean particle size was determined by  $d = (1.12/D) \times 10^{-9}\text{ m} = (1.12/D)\text{ nm}$  [18,19].

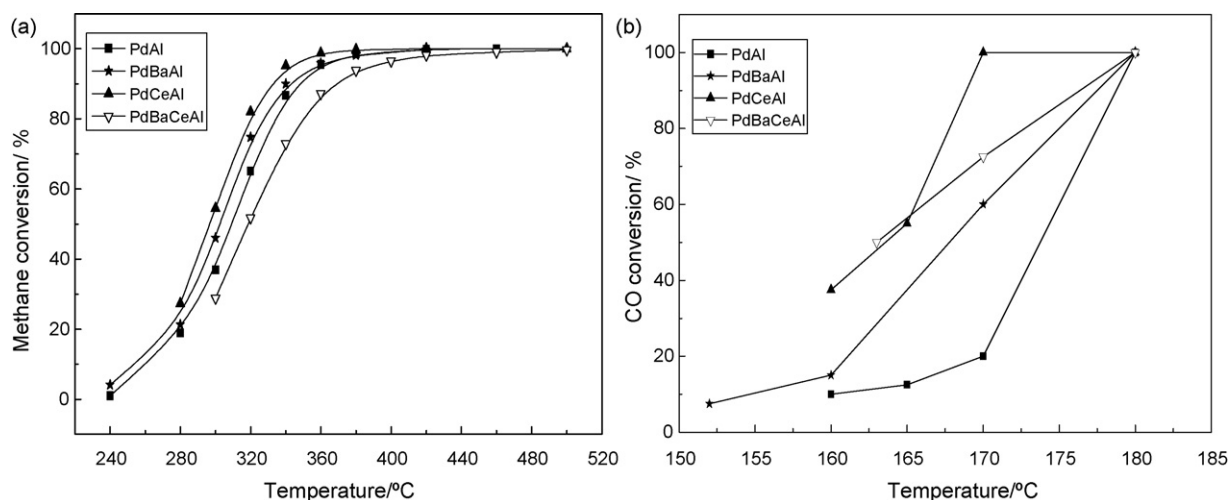
$\text{H}_2$ -TPR was performed on a quartz tubular micro-reactor. 100 mg sample was pretreated in a flow of 10 vol.%  $\text{O}_2/\text{N}_2$  mixture gas (20 ml/min) at  $500^\circ\text{C}$  for 45 min, cooled to room temperature in  $\text{N}_2$  (30 ml/min). The reduction was carried out in a flow of 5 vol.%  $\text{H}_2/\text{N}_2$  mixture (20 ml/min) from room temperature to  $1000^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ . The consumption of  $\text{H}_2$  was detected by TCD.

XPS experiments were carried out on a spectrometer (XSAM-800, KRATOS Co.) with Al  $\text{K}\alpha$  radiation under UHV, calibrated internally by the carbon deposit C 1s binding energy (BE) at 284.8 eV. The uncertainty of binding energy (BE) values is 0.2 eV.

## 3. Results and discussion

### 3.1. Catalytic activity

The results of catalytic activity for methane and CO oxidation over PdAl, PdBaAl, PdCeAl and PdBaCeAl in the simulated exhaust gas are shown in Fig. 1. From the curves of methane oxidation (Fig. 1a), it can be seen that the methane conversion of four catalysts increases continuously with the raising of temperature, and reaches completely conversion above  $400^\circ\text{C}$ . The addition of  $\text{BaO}$  or  $\text{CeO}_2$  increases the catalytic activity for methane conversion under lean-burn condition. But the addition of both  $\text{BaO}$  and  $\text{CeO}_2$  obviously decreases the activity of catalyst under this condition. The data of  $T_{50}$ ,  $T_{90}$  and  $\Delta T = T_{90} - T_{50}$  are obtained from Fig. 1a, and listed in Table 1.  $T_{50}$ ,  $T_{90}$  and  $\Delta T$  are used to evaluate the performances of catalysts. The light-off temperature ( $T_{50}$ ) and completely conversion temperature ( $T_{90}$ ) is the temperature at which a given pollutant conversion reaches 50% and 90%, respectively.  $\Delta T$  is the temperature range from  $T_{50}$  to  $T_{90}$ . It is found that all catalysts exhibit excellent catalytic performances for methane oxidation.  $T_{50}$  and  $T_{90}$  for PdAl are about  $309$  and  $347^\circ\text{C}$ , respectively. For catalyst



**Fig. 1.** Methane (a) and CO (b) conversion versus temperature over PdAl, PdBaAl, PdCeAl, and PdBaCeAl catalysts in the simulated exhaust gas: CH<sub>4</sub> 0.063 vol.%, CO 0.40 vol.%, NO 0.063 vol.%, O<sub>2</sub> 5 vol.%, and CO<sub>2</sub> 12 vol.%, N<sub>2</sub> as balance gas.

PdBaAl,  $T_{50}$  and  $T_{90}$  are 303 and 340 °C, exhibiting better activity for methane oxidation. The minimum values of  $T_{50}$  (295 °C) and  $T_{90}$  (333 °C) for methane are obtained on PdCeAl, indicating that CeO<sub>2</sub> facilitates the methane oxidation effectively. The  $\Delta T$  of PdAl, PdBaAl and PdCeAl is 38, 37 and 38 °C, respectively as shown in Table 1. The small value of  $\Delta T$  suggests that CH<sub>4</sub> reaches completely conversion as soon as it is lighted-off, indicating that these catalysts exhibit remarkably excellent temperature properties. And the value is even much smaller than that of HC from gasoline vehicles [20]. Combining with the difficulty of CH<sub>4</sub> conversion, the result of  $\Delta T$  has particular significance for the industrial application of PdAl, PdBaAl and PdCeAl. The activity results in present work are better than that reported in the literatures associated with CH<sub>4</sub> conversion [7,21], suggesting that the catalysts have excellent catalytic performances for methane oxidation at low temperature and are suitable to be used for NGVs exhaust purification. But for catalyst PdBaCeAl, the coexistence of BaO and CeO<sub>2</sub> causes the sharp decrease of activity, with the highest  $T_{50}$  and  $T_{90}$  (318 and 369 °C) and the largest  $\Delta T$  (51 °C) in four catalysts. Nevertheless, this result is still better than that reported in Ref. [12].

Fig. 1b presents the activity results for CO oxidation. It can be seen that the CO conversion begins at low temperature and reaches completely conversion very quickly. The data of  $T_{50}$ ,  $T_{90}$  and  $\Delta T$  are listed in Table 1. As shown in Table 1, the catalysts exhibit high activities for CO oxidation and  $\Delta T$  is very small. In the four catalysts, PdCeAl exhibits the best catalytic activities,  $T_{50}$  and  $T_{90}$  are 164 and 169 °C, respectively, and  $\Delta T$  is only 5 °C, which has not been found in literature. But PdAl has the worst activity with the highest light-off and completely conversion temperature, 174 °C for  $T_{50}$  and 179 °C for  $T_{90}$ . For PdBaAl,  $T_{50}$  and  $T_{90}$  are 168 and 177 °C and  $\Delta T$  increases to 9 °C. For PdCeAl,  $T_{50}$  is similar to that of PdCeAl and  $T_{90}$  is same to that of PdBaAl, but  $\Delta T$  is the largest (14 °C). The results indicate that CeO<sub>2</sub> and/or BaO can promote the conversion of CO, especially CeO<sub>2</sub>, which maybe due to the presence of great excess oxygen [22] and is in good agreement with Refs. [23,24].

**Table 1**  
Light-off and completely conversion temperatures for methane and CO oxidation.

Samples	$T_{50}$ (°C)		$T_{90}$ (°C)		$\Delta T$ (°C)	
	CH <sub>4</sub>	CO	CH <sub>4</sub>	CO	CH <sub>4</sub>	CO
PdAl	309	174	347	179	38	5
PdBaAl	303	168	340	177	37	9
PdCeAl	295	164	333	169	38	5
PdBaCeAl	318	163	369	177	51	14

### 3.2. Textural properties and dispersion

The results of BET surface areas and pore properties of supports are summarized in Table 2. It is shown that the specific surface area and the pore volume of Al<sub>2</sub>O<sub>3</sub> support are 138 m<sup>2</sup>/g and 0.46 ml/g, respectively. The addition of BaO into Al<sub>2</sub>O<sub>3</sub> can increase the specific surface area (166 m<sup>2</sup>/g) and pore volume (0.49 ml/g). When the support is modified by CeO<sub>2</sub>, the specific surface area (146 m<sup>2</sup>/g) is slightly increased while pore volume (0.45 ml/g) is almost kept the same. The BET results indicate that CeO<sub>2</sub> can enhance the textural properties of Al<sub>2</sub>O<sub>3</sub>, but is less effective than BaO. This is in good agreement with literature [12]. When BaO and CeO<sub>2</sub> are added simultaneously, the specific surface area increases to 160 m<sup>2</sup>/g, and pore volume decreases to 0.43 ml/g, suggesting that the coexistence of BaO and CeO<sub>2</sub> does not further improve the surface area and pore volume of Al<sub>2</sub>O<sub>3</sub>; the surface area result is different with that of Ref. [12], but is similar to that reported in the literature [9], which has the similar contents of CeO<sub>2</sub> and BaO. According to the data of specific surface areas and pore volume in Table 2, it is found that the results of textural properties are not line relationship with the catalytic activities of catalysts. The support with the largest specific surface area and pore volume is not corresponding to the best catalytic activities of catalyst.

The results of CO-chemisorption of Pd catalysts are also listed in Table 2. It has been reported that palladium dispersion and particle size play an important role in the catalytic activities. Simplício et al. [25] have concluded that the highest dispersion and smallest PdO particle size of Pd catalysts can be resultant in the best catalytic activity for methane oxidation. In Table 2, it is revealed that Pd is well dispersed on PdAl, PdBaAl, PdCeAl, and the mean particle size is small. But for PdBaCeAl, the Pd dispersion decreases abruptly, and Pd particle size increases significantly. These results indicate that only BaO or CeO<sub>2</sub> addition can stabilize the Pd dispersion and maintain small Pd particle size, but the coexistence of CeO<sub>2</sub> and BaO decrease the Pd dispersion and increase Pd particle size, which maybe lead to the decrease of catalytic activity. A good correlation is observed between Pd dispersion and catalytic activity, and the lower dispersion of Pd catalysts should be one of the reasons for poor activity of PdBaCeAl in this study. Also, the results are in good agreement with the conclusion of Ref. [25].

### 3.3. XRD characterization

Fig. 2 shows the XRD patterns of PdAl, PdBaAl, PdCeAl and PdBaCeAl. Active  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase are observed in all prepared mate-





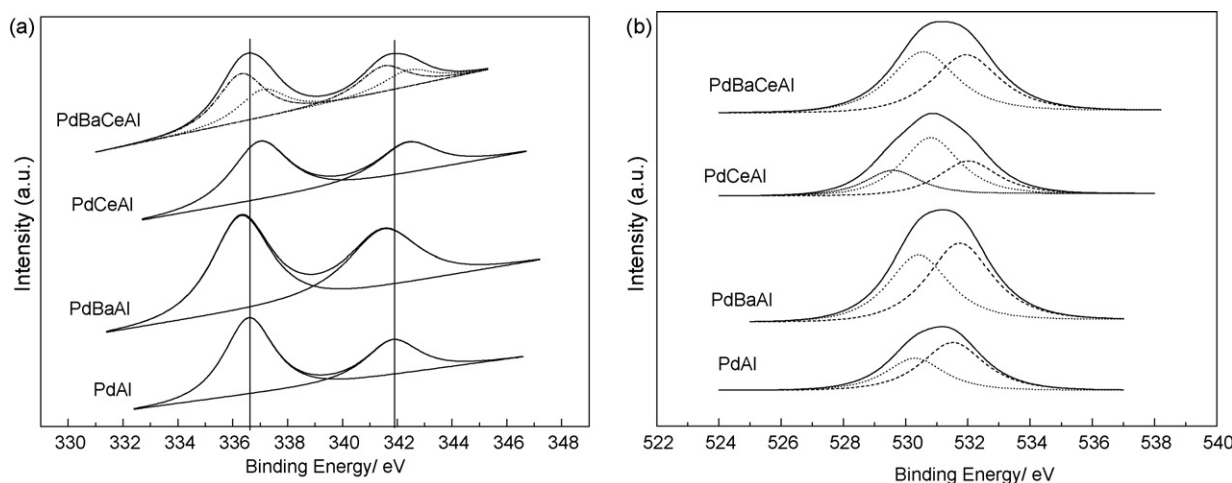


Fig. 4. Pd 3d (a) and O 1s (b) XPS spectra of PdAl, PdBaAl, PdCeAl, and PdBaCeAl catalysts.

### 3.5. XPS results

In order to investigate the effect of BaO and CeO<sub>2</sub> on Pd catalysts in depth, XPS is used to characterize the electronic state of Pd and the surface composition of catalysts. Tables 3 and 4 summarize the binding energy (BE) values and the surface atomic ratios calculated from XPS for four catalysts. Fig. 4a and b shows the XPS spectra lines of Pd 3d and O 1s after edited by XPSPEAK, respectively.

The BE values of the Pd 3d<sub>5/2</sub> are assigned to PdO [15,31], indicating that the palladium species in the four catalysts are PdO, which is more active than metal Pd. Compared with PdAl, the doping of BaO makes the Pd 3d peaks (seen Fig. 4a) shift to lower BE by 0.3 eV, while the doping of CeO<sub>2</sub> makes them shift to higher BE value by 0.4 eV. For the PdBaCeAl catalyst, the Pd 3d peaks are affected by both CeO<sub>2</sub> and BaO, which can be described as the combination of PdBaAl and PdCeAl profiles (seen Fig. 4a and Table 3). From Fig. 4a, it can be seen that the presence of both BaO and CeO<sub>2</sub> change the surface chemical surrounding of PdO, make it more similar to that of PdAl, showing that the effect of BaO or CeO<sub>2</sub> is restrained by each other. This is consistent with the result of TPR.

Fig. 4b and Table 4 show the XPS lines of O 1s and the relative content of O species on the surface. There are mainly two types of surface oxygen species could be recognized from the O 1s XPS lines. The peaks located at 530.0–531.0 eV are assigned to the lattice oxygen (hereafter denoted as O<sub>I</sub>); the other one located at 531.0–532.5 eV (hereafter denoted as O<sub>II</sub>) may be assigned to be the surface hydroxyl groups or the defect oxygen as Refs. [32–34]. For sample PdCeAl, there is also another peak located at 529.6 eV which is assigned to the oxygen species binding with Ce. From the results in Table 4, it can be found that, after modified by BaO or CeO<sub>2</sub>, the binding energies (BE) of O 1s shift to higher value. The BE value of O 1s for PdBaCeAl is higher than that of PdAl, but dose not shift to higher value compared with PdCeAl and PdBaAl, which should be due to the co-effect of BaO and CeO<sub>2</sub>. From Table 4, it is also observed that the oxygen species content on the surface is increased and the

relative ratio of O<sub>I</sub> and O<sub>II</sub> is changed. For the sample without CeO<sub>2</sub>, the O<sub>II</sub> is primary although BaO increases the O<sub>I</sub> content of PdBaAl. Nevertheless, CeO<sub>2</sub> significantly increase the proportion of O<sub>I</sub> (lattice oxygen) on the surface. PdCeAl possesses the highest relative ratio of O<sub>I</sub>, and is most active for methane oxidation, suggesting that lattice oxygen plays an important role in catalytic reaction. However, it should be pointed out that PdBaCeAl holds the second large amount of O<sub>I</sub> in four catalysts but has the worst activity. This can be illustrated by combining with the results of TPR and Pd atom ratio on the surface. The fact that the reduction of PdO and CeO<sub>2</sub> is more difficult reveals lower oxygen mobility of PdBaCeAl. In addition, as displayed in Table 3, the Pd content (0.34%) on the surface is the smallest. These may cause the poor activity of PdBaCeAl.

As reported in Refs. [15,35], the addition of Ba could increase the electron density around PdO as an electron donor, resulting in the decrease of BE value and enhancing the thermal stability of PdO. In present paper, combining with the results of CO-chemisorption and H<sub>2</sub>-TPR, it can be concluded that the PdO–BaO interaction can stabilize the PdO dispersion and improve the redox ability of PdO/Pd, thus leading to the better catalytic activity for methane oxidation. The doping of CeO<sub>2</sub> increases the BE values of Pd 3d peaks, which is owing to the strong interaction of PdO with CeO<sub>2</sub> and CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support system, as reported in Refs. [31,36,37]. When CeO<sub>2</sub> is present, the atom ratio of O to Pd (200:1) is increased greatly compared with that of PdAl (132:1) and the percentage of lattice oxygen is also increased, as shown by the results of O 1s. These results indicate that more active oxygen surrounds PdO phase, thus accelerate the reduction of PdO and enhance catalytic activity for methane oxidation. However, in the case of BaO and CeO<sub>2</sub> added into the support simultaneously, CeO<sub>2</sub> species cannot be detected on the surface of PdBaCeAl by XPS, it can be inferred that the interaction of PdO–CeO<sub>2</sub> is weaker, which is resultant in the enhancement of reduction temperature (Fig. 3). The surface composition of atoms also change. These findings suggest that BaO alter the chemical surroundings of PdO and CeO<sub>2</sub>. The decrease of CeO<sub>2</sub> and PdO contents on the surface reveals that more PdO and CeO<sub>2</sub> enter into the bulk of Al<sub>2</sub>O<sub>3</sub> support. These results indicate that the addition of BaO changes the distribution of CeO<sub>2</sub> in support, weakens the mutual interaction of PdO and surface CeO<sub>2</sub>. Similarly, the interaction between PdO and BaO is also weakened owing to the presence of CeO<sub>2</sub>. As a result, the catalytic activity for methane and CO oxidation decreases rapidly. Based on the above results, it can be concluded that the strong interaction between PdO and additives plays an important role in promoting catalytic activity. But the coexistence of BaO and CeO<sub>2</sub> does not give the expected synergistic effect.

Table 4  
The binding energy and surface composition results of O 1s for four catalysts.

Samples	O 1s			O:Pd (atom)
	BE (eV)	at%	O <sub>I</sub> /O <sub>II</sub> (at%)	
PdAl	530.3 (531.2)	62.00	38.2/61.8	132
PdBaAl	530.4 (531.7)	66.46	44.6/55.4	148
PdCeAl	530.8 (532.0)	77.99	63.3/36.7	200
PdBaCeAl	530.6 (531.9)	65.35	51.4/48.6	192

#### 4. Conclusions

In this study, palladium supported catalysts used for lean-burn natural gas vehicles (NGVs) have been prepared and investigated. The activity results indicate that the catalysts have excellent performances for methane and CO removal at low temperature under lean condition, and have great potential to industrial application. Among them, PdCeAl shows the best activity but PdBaCeAl the worst. It is found that the catalytic activity is strongly affected by the interaction of PdO and additives. BaO or CeO<sub>2</sub> each could stabilize palladium dispersion, enhance the reducibility of palladium catalyst and increase the catalytic activity for methane and CO oxidation. BaO and CeO<sub>2</sub> influence the properties of catalysts by different ways: the former is effective as an electron donor, increasing the electron density around PdO; the latter is acted owing to its strong mutual interaction with PdO on the surface and its ability of activating oxygen and increasing oxygen mobility. Nevertheless, in the case of BaO and CeO<sub>2</sub> added simultaneously, BaO makes CeO<sub>2</sub> enter into the bulk of Al<sub>2</sub>O<sub>3</sub> and cannot be detected on the surface, which weakens the interaction of PdO–CeO<sub>2</sub>. Similarly, the electronic effect of BaO is also weakened by CeO<sub>2</sub>. The coexistence of BaO and CeO<sub>2</sub> restrains the beneficial effect with each other and cannot give the expected synergistic effect, leading to the worst catalytic activity for methane oxidation.

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