



Effects of Ce on catalytic combustion of methane over Pd-Pt/Al₂O₃ catalyst

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Abstract

Activity and stability of 1%Pd-0.2%Pt/Al₂O₃ and 1%Pd-0.2%Pt/0.6%Ce/Al₂O₃ catalysts prepared by impregnation method for catalytic combustion of methane in air were investigated. The catalysts before and after reaction were characterized by BET, CO chemisorption, XRD and XPS techniques. Results showed that the presence of Ce significantly increased the activity and thermal stability of the Pd-Pt/Al₂O₃ catalyst towards methane combustion, which could be attributed to more highly-dispersed active PdO particles over the Pd-Pt/Ce/Al₂O₃ catalyst surface as well as the retarded sintering of PdO and the maintained oxidized state of surface Pd during the combustion process in the presence of Ce.

Key words: catalytic combustion; methane; Pd-Pt/Ce/Al₂O₃ catalyst; stability; metal dispersion

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Introduction

Low-concentration methane widely exists in industrial exhaust gases and natural gas vehicles. It is a well-known greenhouse gas and should be removed before emission (Li et al., 2009). In recent years, catalytic methane combustion over Pd-based catalysts has been widely investigated due to the high combustion activity, with PdO being the main active phase under lean combustion conditions (Epling and Hoflund, 1999; Sekizawa et al., 2000; Groppi et al., 2001; Xiao et al., 2004; Guerrero et al., 2006; Roth et al., 2006; Ferrer et al., 2009; Specchia et al., 2009; Castellazzi et al., 2010). However, the Pd-based catalysts suffer from serious deactivation during the reaction. Modifications of the Pd-based catalysts seem necessary to improve the catalytic stability for practical applications (Liotta et al., 2002; Ozawa et al., 2003; Yue et al., 2005a, 2005b).

As an attractive alternative, a bimetallic Pd-Pt system proved to prolong the catalyst lifetime for methane combustion (Narui et al., 1999; Ozawa et al., 2004a; Strobel et al., 2005; Persson et al., 2005, 2006, 2007). On the other hand, it has been suggested that the presence of some rare earth elements such as Ce, La, Nd, Sm and Y also improves the thermal stability of Pd-based catalysts, mainly via preventing the growth and decomposition of PdO particles during the combustion (Arai and Machida, 1996; Ozawa et al., 2004b; Xiao et al., 2005; Yue et al., 2005b). Among these rare earth elements, Ce is considered to be especially appropriate due to the oxygen storage capability of CeO₂, affecting the redox properties of the catalysts (Deng and

Neveall, 1999; Xiao et al., 2005; Colussi et al., 2007).

In the present study, Ce, Pd, and Pt were successively loaded on alumina by impregnation method for catalytic combustion of methane. The activity and stability of Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts were comparatively studied. To explain the observed results, the physicochemical properties of the two catalysts were investigated using BET, CO chemisorption, XRD and XPS techniques.

1 Experimental

1.1 Catalyst preparation

Ce/Al₂O₃ was firstly prepared by impregnation of γ -Al₂O₃ powder (Sinopharm Chemical Reagent Co., Ltd., China, 40–60 mesh, BET surface area 228.3 m²/g, pore volume 0.4149 cm³/g) with an aqueous solution of Ce(NO₃)₃·6H₂O (Tianjin Jinke Fine Chemical Research Institute, China, 99% purity) with stirring at 60°C. The impregnated sample was dried at 110°C for 12 hr, and then calcined in air at 550°C for 4 hr. The theoretical content of Ce was 0.6 wt.%.

To prepare Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts, Al₂O₃ and Ce/Al₂O₃ were separately impregnated with aqueous solutions of Pd(NO₃)₂·2H₂O (Shenyang Jinke Reagent Factory, China, Pd metal content 39.5%) with stirring at 60°C. The impregnated samples were dried at 110°C for 12 hr, and then calcined in air at 550°C for 4 hr. The resulting samples were impregnated with aqueous solutions of H₂PtCl₆·6H₂O (Shenyang Jinke Reagent Factory, China, Pt metal content 37%) with stirring at

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60°C, dried at 110°C for 12 hr, and then calcined in air at 550°C for 10 hr. The theoretical contents of Pd and Pt were 1 wt.% and 0.2 wt.%, respectively.

1.2 Catalytic testing

Catalytic methane combustion was carried out in a conventional continuous-flow fixed-bed reactor (U-shaped quartz tube of 6 mm I.D.) placed inside a programmable temperature-controlled furnace. The loading amount of catalyst was 0.5 g. A gas mixture of 1.5 vol.% CH₄ in dry air was introduced into the reactor at a flow rate of 940 mL/min (space velocity of 80,000 hr⁻¹) under atmospheric pressure. Methane in the feed and exhaust gases was analyzed using an online Agilent HP-6890N GC (USA), equipped with a thermal conductivity detector (TCD) and a 2-m TDX-01 (carbon molecular sieve) packed column (2 mm I.D.). The conversion of methane was calculated based on its inlet and outlet concentrations. During the catalytic activity tests, the methane conversion was measured as a function of temperature varied from 250 to 500°C by steps of 25°C (heating rate: 5°C/min) with 15 min temperature hold between each heating ramp step. During the catalytic stability tests, the methane conversion was measured as a function of time on stream at a constant temperature of 400°C. Prior to catalytic testing, the catalysts were treated in air at 500°C for 2 hr, and then cooled to 250 or 400°C for the catalytic activity and stability tests, respectively.

1.3 Catalyst characterization

The BET surface areas of the catalysts were calculated from the nitrogen adsorption isotherms at -196°C measured with a NOVA 2200e instrument. Prior to the adsorption measurements, the catalysts were degassed in vacuum at 250°C for at least 2 hr.

The metallic surface areas of the catalysts were calculated from the CO chemisorptions measured using an Autochem II 2920 automated chemisorption analyzer (Micromeritics, USA), based on the assumption that the amount of CO molecules adsorbed on the catalyst equals the number of metallic active sites (metal atoms) over the catalyst surface. Before measuring the CO adsorption, the catalysts were reduced in H₂ (99.99%, 20 mL/min) at 500°C for 1 hr, purged with He (99.99%, 20 mL/min) at 520°C for 1 hr, and then cooled down to 50°C in He flow (20 mL/min).

X-ray diffraction (XRD) patterns of the catalysts were collected on a Rigaku D/max-2200 diffractometer (Cu K α radiation, 40 mA, 40 kV, 2 θ : 20°–80°). The crystallite sizes of PdO over the catalysts were calculated by Scherrer's equation with the FWHM (full width at half maximum) values of the characteristic peak of PdO (at 2 θ = 33.7°).

X-ray photoelectron spectroscopies (XPS) were acquired on a ThermoFisher Scientific ESCALAB 250 electron spectrometer operating with monochromatized Al K α radiation (120 W). After a survey scan in the range of 0–1350 eV, the binding energy regions of 65–87 eV (Al 2p), 277–296 eV (C 1s), 332–347 eV (Pd 3d), and 522–542 eV (O 1s) were scanned in detail, taking the C 1s line (284.8 eV) of adventitious carbon as reference. The pass

energies for survey and detailed scans were 200.0 and 30.0 eV, respectively.

2 Results and discussion

2.1 Catalytic activity

The methane conversion over Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts plotted as a function of reaction temperature is shown in Fig. 1. It can be seen that the methane conversion over both catalysts increased with the increase of reaction temperature. On the other hand, the presence of Ce significantly improved the activity of Pd-Pt/Al₂O₃ catalyst for methane combustion. The temperatures for 50% conversion of methane (T_{50}) were 362 and 342°C for Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts, respectively.

2.2 Catalytic stability

Figure 2 presents the methane conversion over Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts at 400°C as a function of time on stream. The two catalysts showed almost the same initial activity towards methane combustion. However, the methane conversion over the Pd-Pt/Al₂O₃ catalyst underwent a sharp decrease

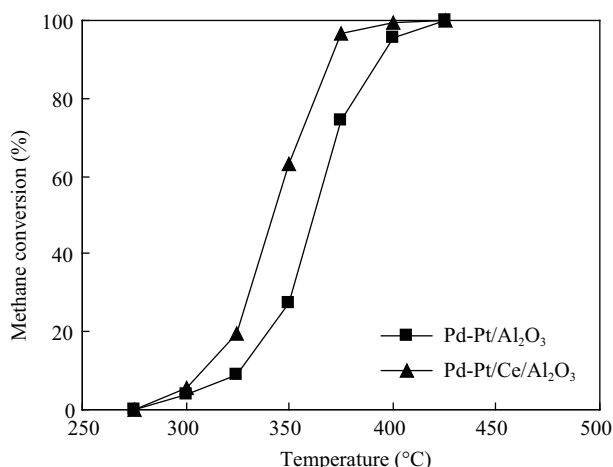


Fig. 1 Methane conversion over Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts as a function of reaction temperature.

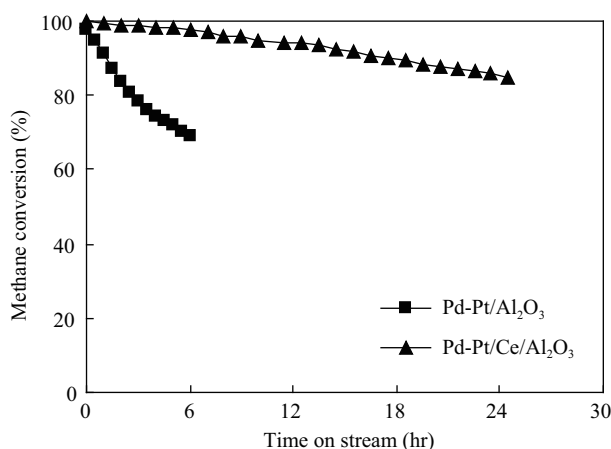


Fig. 2 Methane conversion over Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts as a function of time on stream. Reaction temperature: 400°C.

with time on stream while that over the Pd-Pt/Ce/Al₂O₃ catalyst only experienced a slight decrease. As a result, the lifetime of the Pd-Pt/Ce/Al₂O₃ catalyst, corresponding to a 15% decline of the methane conversion from the start, was 24.5 hr, much longer than that of the Pd-Pt/Al₂O₃ catalyst (2.2 hr). Considering the expensive cost of noble metals, the significant prolonging of the catalyst lifetime by modifying the Al₂O₃ support with Ce is of considerable economic significance for practical applications of the catalyst.

2.3 Catalyst properties

2.3.1 BET surface area and metallic surface area

Table 1 presents the BET and metallic surface areas of Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts before and after reaction. The BET surface area (m²/g catalyst) includes the surface areas of both the support and the active species such as PdO, Pd and Pt. The surface area of the active species is correlated to the number of active sites measured by the CO chemisorption, and is characterized by the metallic surface area (m²/g metal) in this study.

As shown in Table 1, the Ce-modification slightly reduced the BET surface area of the fresh catalyst but significantly increased the metallic surface area. This result suggests that the presence of Ce increases the number of active sites over the catalyst surface although it reduces the surface area of the support. These increased active sites should be mainly responsible for the improved catalytic activity of Pd-Pt/Ce/Al₂O₃ (Fig. 1). On the other hand, the BET and metallic surface areas of the two catalysts declined after reaction at 400°C for 10 hr. The number of active sites decreased during the combustion processes, partly explaining the decreasing methane conversion with time on stream (Fig. 2). As compared to the Pd-Pt/Al₂O₃ catalyst, however, the presence of Ce significantly retarded the loss of active sites, resulting in better stability of the Pd-Pt/Ce/Al₂O₃ catalyst (Fig. 2).

2.3.2 XRD spectra

Figure 3 shows the XRD spectra of Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts before and after reaction. From the XRD analysis, PdO ($2\theta = 33.7^\circ, 42.1^\circ$) was formed over the two catalysts. No peak correlated to Pt or Ce was observed, probably due to the relatively low contents and/or the high dispersion of Pt and Ce over the catalysts.

The FWHM values of the characteristic peak of PdO ($2\theta = 33.7^\circ$) and the calculated PdO crystallite sizes are listed in Table 2. For fresh catalysts, a larger FWHM value and a smaller PdO crystallite size were observed

Table 1 BET surface areas and metallic surface areas of Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts before and after reaction

Catalyst	BET surface area ^a (m ² /g)		Metallic surface area ^b (m ² /g)	
	Fresh	Reacted ^c	Fresh	Reacted ^c
Pd-Pt/Al ₂ O ₃	194.4	150.5	53.8	28.3
Pd-Pt/Ce/Al ₂ O ₃	172.1	145.8	64.6	43.6

^a Based on the catalyst weight; ^b based on the Pd and Pt metal weight; ^c after reaction at 400°C for 10 hr.

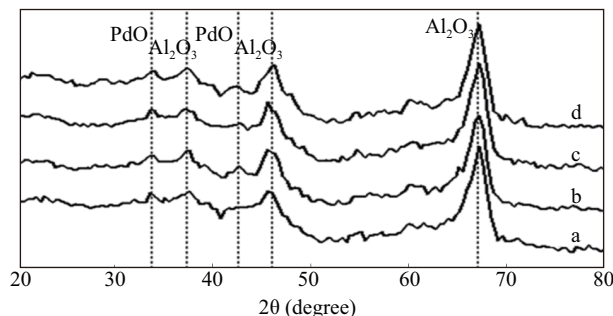


Fig. 3 XRD spectra of different catalysts. (line a) fresh Pd-Pt/Al₂O₃ catalyst; (line b) fresh Pd-Pt/Ce/Al₂O₃ catalyst; (line c) Pd-Pt/Al₂O₃ catalyst after reaction at 400°C for 10 hr; (line d) Pd-Pt/Ce/Al₂O₃ catalyst after reaction at 400°C for 10 hr.

Table 2 FWHM values of the characteristic peak of PdO ($2\theta = 33.7^\circ$) and the calculated PdO crystallite sizes for Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts before and after reaction

Catalyst	FWHM		PdO crystallite size ^a (nm)	
	Fresh	Reacted ^b	Fresh	Reacted ^b
Pd-Pt/Al ₂ O ₃	0.742	0.514	11.3	16.4
Pd-Pt/Ce/Al ₂ O ₃	0.884	0.850	9.5	9.8

^a Calculated by Scherrer's equation with the FWHM value; ^b after reaction at 400°C for 10 hr. FWHM: full width at half maximum.

for Pd-Pt/Ce/Al₂O₃ than for Pd-Pt/Al₂O₃, implying that active particles were in higher dispersion in the presence of Ce, leading to the increased metallic surface area of Pd-Pt/Ce/Al₂O₃ with respect to Pd-Pt/Al₂O₃ (Table 1). On the other hand, decrease in the FWHM value and increase in the PdO crystallite size were observed for the two catalysts after reaction at 400°C for 10 hr, suggesting that sintering of PdO occurred for both catalysts during the methane combustion, partially explaining the decrease of metallic surface area after reaction (Table 1). However, the changes in the FWHM value and in the PdO crystallite size for Pd-Pt/Ce/Al₂O₃ were much smaller than those for Pd-Pt/Al₂O₃. The presence of Ce effectively retarded the sintering of PdO particles and thus improved the thermal stability of the catalyst for methane combustion (Fig. 2).

2.3.3 XPS analysis

In order to determine the oxidation states of Pd and the relative contents of each state over the catalysts surface, the XPS Pd 3d spectra were deconvoluted using the XPS peak v4.1 software based on the binding energies reported in the literature (335.2, 336.7 and 337.5 eV for Pd⁰, Pd²⁺ and Pd⁴⁺, respectively) (Persson et al., 2007), as shown in Fig. 4. The binding energies of Pd (3d_{5/2}), the oxidation states of Pd, the relative contents of each Pd state, and the surface atomic ratios of Pd to Al (calculated from the peak areas of Pd 3d and Al 2p) are compiled in Table 3.

All three oxidation states (Pd⁰, Pd²⁺ and Pd⁴⁺) were observed over the fresh Pd-Pt/Al₂O₃ catalyst while only Pd²⁺ and Pd⁴⁺ were present over the fresh Pd-Pt/Ce/Al₂O₃ catalyst (Table 3). The presence of Ce seems to suppress the formation of Pd⁰, which is generally known to have lower activity during combustion as compared to PdO (Ozawa et al., 2004a; Persson et al., 2007). A mixture of Pd⁰ and Pd²⁺ remained over the Pd-Pt/Al₂O₃ catalyst

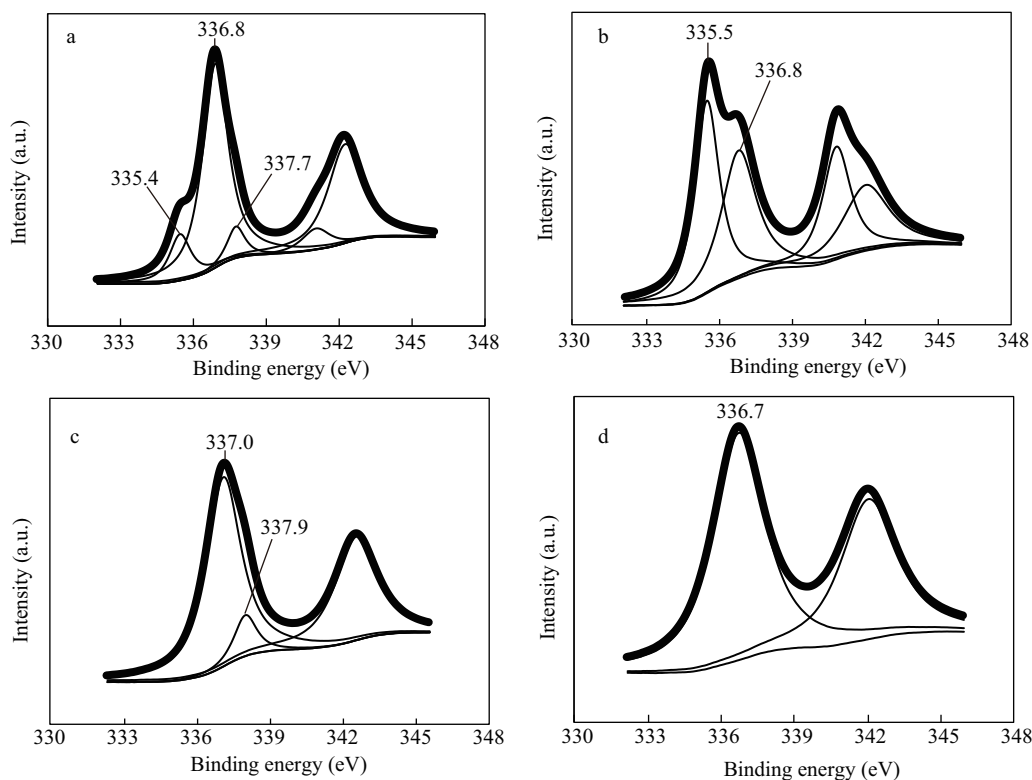


Fig. 4 XPS Pd 3d spectra of different catalysts. (a) fresh Pd-Pt/Al₂O₃ catalyst; (b) Pd-Pt/Al₂O₃ catalyst after reaction at 400°C for 10 hr; (c) fresh Pd-Pt/Ce/Al₂O₃ catalyst; (d) Pd-Pt/Ce/Al₂O₃ catalyst after reaction at 400°C for 24.5 hr.

Table 3 Binding energies of Pd (3d_{5/2}), oxidation states of Pd, relative contents of each Pd state, and surface Pd/Al ratios for Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts before and after reaction

Catalyst	Pd (3d _{5/2}) (eV)	Oxidation state	Relative content (%)	Surface Pd/Al ratio
Fresh Pd-Pt/Al ₂ O ₃	335.4	Pd ⁰	14.4	0.009
	336.8	Pd ²⁺	77.4	
	337.7	Pd ⁴⁺	8.2	
Reacted Pd-Pt/Al ₂ O ₃ ^a	335.5	Pd ⁰	52.0	0.007
	336.8	Pd ²⁺	48.0	
Fresh Pd-Pt/Ce/Al ₂ O ₃	337.0	Pd ²⁺	87.8	0.011
	337.9	Pd ⁴⁺	12.2	
	336.7	Pd ²⁺	100	
Reacted Pd-Pt/Ce/Al ₂ O ₃ ^b	336.7	Pd ²⁺	100	0.008

^a After reaction at 400°C for 10 hr; ^b after reaction at 400°C for 24.5 hr.

after reaction at 400°C for 10 hr while only Pd²⁺ was present over the Pd-Pt/Ce/Al₂O₃ catalyst after reaction at 400°C for 24.5 hr. Pd⁴⁺ over both catalysts disappeared during the combustion processes, probably due to its extremely low stability (Persson et al., 2007). In addition, it is worth mentioning that although Pd⁰ and Pd⁴⁺ were detected by XPS, no Pd⁰ or Pd⁴⁺ was detected in the bulk phase by XRD, indicating that Pd⁰ and Pd⁴⁺ were highly dispersed over the catalyst surface.

On the other hand, the relative content of Pd²⁺ over the Pd-Pt/Al₂O₃ catalyst decreased along with a significant increase in the content of Pd⁰ after 10-hr reaction (Table 3), indicating that the transformation of PdO to metallic Pd occurred over the Pd-Pt/Al₂O₃ catalyst during the combustion. After the Ce-modification, however, the surface Pd was kept at the oxidized state after 24.5-hr reaction, suggesting that the metallic Pd was readily reoxidized to PdO during the reaction in the presence of Ce (Yasuda et al., 2011), well explaining the observed better stability of the Pd-Pt/Ce/Al₂O₃ catalyst (Fig. 2). These results confirm

that PdO is the active phase for methane combustion over the bimetallic Pd-Pt catalysts. Besides, results presented in Table 3 also show that the surface Pd/Al ratios over both catalysts dropped after reaction. Nevertheless, the average dropping rate over the Pd-Pt/Ce/Al₂O₃ catalyst (1.1%/hr) was much lower than that over the Pd-Pt/Al₂O₃ catalyst (2.2%/hr). This observation implies that the presence of Ce significantly restrained the loss of Pd species during methane combustion, being in agreement with the result of CO chemisorption.

In summary, the sintering of PdO, the decrease of the valence of surface Pd and the loss of Pd species all contribute to the catalyst deactivation. Comparison of these changes during the combustion process between Pd-Pt/Al₂O₃ and Pd-Pt/Ce/Al₂O₃ catalysts indicates that the presence of Ce has much more significant effects on preventing the PdO sintering and keeping the surface Pd at the oxidized state than on restraining the loss of Pd species. Therefore, the improved stability of the Pd-Pt/Ce/Al₂O₃ catalyst could be mainly attributed to the stabilized PdO dispersion and the

maintained oxidized state of surface Pd in the presence of Ce.

3 Conclusions

The 1%Pd-0.2%Pt/Al₂O₃ and 1%Pd-0.2%Pt/0.6%Ce/Al₂O₃ catalysts were prepared by impregnation method for catalytic combustion of methane in air. The Pd-Pt/Ce/Al₂O₃ catalyst exhibits improved activity and stability towards methane combustion compared with the Pd-Pt/Al₂O₃ catalyst. Characterization results show that Ce-modification of the Al₂O₃ support promotes the activity of the Pd-Pt/Al₂O₃ catalyst by increasing the dispersion of active PdO particles over the catalyst surface, and improves the catalyst stability mainly via preventing the sintering of PdO and keeping the surface Pd at the oxidized state during the combustion process.

Acknowledgments

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