

Effect of Addition of Pt, La₂O₃, Nd₂O₃ and ZrO₂ to PdO/Al₂O₃ on Catalytic Combustion of Methane

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The addition of Pt prolongs the lifetime of the PdO/Al₂O₃ catalyst during CH₄ combustion at 1073 K. Furthermore, the addition of ZrO₂, La₂O₃ and Nd₂O₃ greatly extends the lifetime of the Pt–PdO/Al₂O₃ catalyst. This is due not to the transformation of PdO to Pd–Pt but to the prevention of the growth of PdO particles during the reaction.

Catalytically-assisted combustion of methane has the potential to reduce thermal NO_x emissions from gas turbine combustors.¹ Palladium supported on alumina is one of the most active catalysts for methane combustion, however, its poor durability has hindered the development of catalytic combustors. Deactivation of the catalyst is mainly due to a decrease in the surface area of alumina² and the transformation of PdO to Pd³ at high temperature. The addition of La stabilizes the surface area of alumina and does so more effectively than Nd.⁴ Few studies have been made on the synergistic effect of the addition of both La and Nd to PdO/Al₂O₃ on catalyst deactivation in CH₄ combustion. Narui et al.⁵ reported that the addition of ZrO₂ to Al₂O₃ prevented the transformation of PdO to Pd, but Farrauto et al.⁶ found a contrary result. Kuper et al.⁷ reported that Pt had no transition temperature but the addition of Pt to PdO promoted the transformation of PdO to Pd. Thus, the effect of the addition of Pt to PdO/Al₂O₃ has not been fully understood. Furthermore, little attention has been paid to the addition of La, Nd and Zr to Pt–PdO/Al₂O₃. In this study, we report that the addition of Pt forms a Pd–Pt alloy and prevents the growth of PdO and that the addition of La, Nd and Zr significantly prevents the growth on Pt–PdO/Al₂O₃ during CH₄ combustion. Furthermore, TPD after CH₄ adsorption characterizes the stability of PdO.

Catalysts composed of PdO and Al₂O₃, and/or Pt, Nd₂O₃, La₂O₃ and ZrO₂ were prepared (Table 1). γ -Alumina powder (BET surface area 94 m²·g^{−1}) was impregnated with aqueous solutions of Nd(NO₃)₃·6H₂O, La(NO₃)₃·6H₂O with stirring, dried at 383 K for 1 h, and then calcined at 1273 K for 2 h. The resulting solid and ZrO₂ powder (surface area 101 m²·g^{−1}) were mixed and impregnated with aqueous solutions of Pd(NO₃)₂, dried at 383 K for 1 h, calcined at 1073 K for 2 h, cooled to room temperature, and then impregnated with aqueous solutions of H₂PtCl₆·6H₂O and calcined by the same procedure. For the measurement of methane combustion, the solids

were molded, crushed and sieved to 9–16 mesh. The CH₄ combustion was carried out in a conventional fixed-bed flow reactor with 0.30 g of the catalyst at atmospheric pressure. 1.0 vol% CH₄/air was introduced into the reactor at 450 l·h^{−1}. The catalyst was heated to 1073 K at the rate of 10 K·min^{−1}, then kept for 10 h (or 5 min) at 1073 K for the deactivation measurement. For TPD measurement, the catalyst was heated from room temperature to 1273 K at a rate of 10 K·min^{−1} in a stream of He after the catalyst had been flowed in a stream of air at 673 K for 3 h and in a stream of CH₄ at room temperature for 5 min. Gases desorbed during TPD were analyzed with a quadrupole mass spectrometer (Prisma QMS200, Balzers Co.). The XRD spectra of the catalysts before and after CH₄ combustion were taken and identified using ASTM cards.

From the XRD analysis, PdO was observed for all the catalysts before the combustion. Metallic Pd was not observed for PdO/Al₂O₃, but Pd–Pt alloy was identified by its XRD reflection at $2\theta = 39.9^\circ$ for a combined peak of Pt (111) at $2\theta = 39.7^\circ$ and Pd (111) at $2\theta = 40.1^\circ$ for the Pt doped catalysts.⁸ The deactivation behavior was examined to fit a deactivation equation to the CH₄ combustion data taken every 10 min at 1073 K. We proposed the following relationship between activity of PdO/Al₂O₃ and time:⁹

$$\phi = rt/rt_0 = r_1[1/(1 + (\alpha_1 \cdot t))^{n_1} + r_2[1/(1 + \alpha_2 \cdot t)]^{n_2} \quad (1)$$

where rt is combustion rate, rt_0 is initial (5 min) combustion rate, r_i ($i = 1$ and 2), α_i and n_i are constants, and t is time on stream. Eq (1) is derived on the basis of sintering kinetics.¹⁰ The first term of Eq (1) is subject to rapid deactivation species and the second term to slow deactivation species, respectively. The ratios of combustion rate at time on stream to that at 5 min after the start (ϕ) and the fitting result to Eq (1) are shown in Figure 1. ϕ for PdO/Al₂O₃ rapidly dropped to 0.74 at 2 h and then gradually decreased to 0.55 at 10 h. The addition of Pt lowered the deactivation of PdO/Al₂O₃ throughout the time-on-stream, while the addition of ZrO₂, La and Nd prevented the steady-state deactivation of Pt–PdO/Al₂O₃. Furthermore, ϕ for La–Nd–Pt–PdO/Al₂O₃–ZrO₂ at more than 2 h was the highest. Because the value of the chi-squared test was small enough ($0.3 - 2.9 \times 10^{-6}$), Eq (1) fitted the data of ϕ . Regarding the parameters in Eq (1), n is an exponent and has a stronger influence on the deactivation than α . The relationship between the changes in the catalyst properties and the parameters in Eq (1) is shown in Table 2. n_1 was hardly correlated with the catalyst lifetime, the BET surface area and the crystallite size. On the other hand, there was a good correlation among the catalyst lifetime, n_2 and the increase in crystallite size of PdO (101) from 5 min to 10 h. On the contrary, there was a weak correlation between the catalyst lifetime and the decrease in BET surface area from 5 min to 10 h. These results show that the catalyst lifetime was strongly affected by the slow deactivation caused by the growth of PdO. r_1/r_2 is the ratio of the deactivation by rapid deactivation species to that by slow

Table 1. Catalyst composition based on weight

Component	Catalyst								
	1	2	3	4	5	6	7	5B	7B
Pt		5	5	5	5	5	5	5	5
PdO	23	23	23	23	23	23	23	23	23
La ₂ O ₃			3		3		2.4	1.5	1.2
Nd ₂ O ₃				3	3		2.4	1.5	1.2
Al ₂ O ₃	100	100	100	100	100	80	80	100	80
ZrO ₂						20	20		20

Table 2. Physical properties and catalytic activities of La–Nd–Pt–PdO/Al₂O₃–ZrO₂ and parameters for simulated deactivation functions

Properties and parameters	Combustion time	Catalyst								
		1	2	3	4	5	6	7	5B	7B
BET surface area/m ² ·g ⁻¹	5 min ^a	53	48	50	49	46	41	42	49	44
	10 h/5 min ^b	0.88	0.96	0.97	0.96	0.96	0.77	0.87	0.97	0.92
Crystallite size of PdO ^c /nm	5 min ^a	13	15	11	14	12	15	13	15	14
	10 h/5 min ^b	1.3	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0
Crystallite size of Pd–Pt ^c /nm	5 min ^a	— ^d	28	27	28	25	28	27	26	27
	10 h/5 min ^b	32/— ^d	1.1	1.1	1.1	1.0	1.1	1.0	1.1	1.0
Combustion rate /μmol·s ⁻¹ ·g ⁻¹	5 min ^a	145	132	138	133	126	129	126	131	131
	10 h/5 min ^b	0.55	0.66	0.64	0.64	0.70	0.67	0.73	0.69	0.71
$n_1 \times 10^{-6}$		0.11	0.79	0.08	0.37	0.45	0.41	0.04	1.04	0.01
n_2		0.23	0.16	0.13	0.13	0.11	0.09	0.09	0.08	0.07
$(r_1/r_2) \times 10^3$		90	53	57	65	57	75	62	58	61
Catalyst lifetime ^e /h		27	63	102	81	175	233	457	599	1736

^aAt 5 min after the start of combustion at 1073 K. ^bThe ratio of the value at 10 h to that at 5 min. ^cCalculated by the Scherrer's equation with the peak width of PdO (101) or Pd–Pt (111) in XRD. ^dCrystallite size of Pd. ^eConversion of 35%.

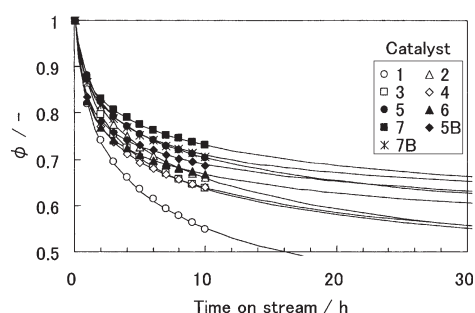


Figure 1. Ratio of combustion rate of CH₄ and simulation at 1073 K with time on stream. Combustion conditions: CH₄ = 1 vol%, air = 99 vol%, CH₄/air flow = 450 l·h⁻¹, catalyst weight = 0.3 g.

deactivation species. The ratio r_1/r_2 was hardly correlated to the decrease in BET surface area. Additionally, we found that the rapid deactivation of PdO/Al₂O₃ was caused by the transformation of PdO to metallic Pd.⁹ As a result, the Pt doped PdO/Al₂O₃ catalysts were rapidly deactivated by the transformation of PdO to Pd–Pt. Therefore, the ratio of r_1/r_2 shows the ratio of deactivation by the transformation of PdO to that by the growth of PdO. As shown in Table 2, the addition of Pt decreased the catalyst activity at 5 min after the start but prevented both the growth and the transformation of PdO. The addition of ZrO₂ to Pt–PdO/Al₂O₃ increased the transformation of PdO, which is in agreement with the result obtained by Farrauto et al.,⁶ but prevented the growth of PdO. The addition of La or Nd alone increased the transformation of PdO but maintained the crystallite size of PdO from 5 min to 10 h. The addition of both La and Nd had a stronger effect on preventing the growth of PdO and Pd–Pt alloy than that of La or Nd alone. These results show the synergistic effect of addition of both La and Nd on the prevention of PdO growth. In order to confirm the effect of the addition of Pt, ZrO₂, La and Nd on the transformation of PdO, TPD of O₂ desorption after CH₄ adsorption was carried out (Figure 2). Oxygen was desorbed from PdO owing to rupture of the Pd and O bond of PdO.¹¹ For PdO/Al₂O₃, the O₂ desorption was observed to reach a peak at 873 K. The addition of Pt to PdO/Al₂O₃ shifted the peak to 1125 K, indicating the prevention of the transformation of PdO to Pd, which is contrary to the result obtained by Kuper et al.⁷ A small amount of Pt addition would prevent the transformation. The

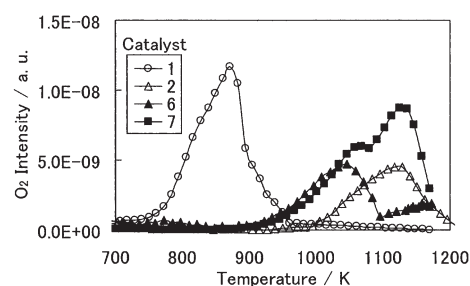


Figure 2. TPD profiles of O₂ desorption after CH₄ adsorption.

addition of ZrO₂ to Pt–PdO/Al₂O₃ shifted the peak to 1050 K and promoted the transformation of PdO. The addition of both La and Nd to Pt–PdO/Al₂O₃–ZrO₂ shifted the peak to 1130 K with a shoulder peak at 1070 K to prevent the transformation of PdO. These results support the simulation result that the rapid deactivation was caused by the transformation of PdO to Pd and consequent release of oxygen.

In conclusion, the lifetime of PdO/Al₂O₃ and Pt–PdO/Al₂O₃ catalysts during CH₄ combustion at 1073 K is affected more by the particle growth of PdO than by the transformation of PdO to metallic Pd or Pd–Pt alloy. The particle growth of PdO was strongly lowered by the addition of Pt, ZrO₂, La and Nd. The transformation of PdO was decelerated by the addition of Pt but accelerated by that of ZrO₂. The La–Nd–Pt–PdO/Al₂O₃–ZrO₂ catalyst showed a much longer lifetime than the other catalysts.

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