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Oxidation of methane over Pt and Pd supported on alumina in lean-burn natural-gas engine exhaust

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Abstract

Catalytic oxidation of hydrocarbons in lean-burn natural-gas engine exhaust has been studied for Pt and Pd supported on alumina. A Pt–Pd/alumina catalyst exhibited higher and longer-lasting hydrocarbon oxidation activity than Pt–Rh/alumina, Pt/alumina, and Pd/alumina catalysts. Increasing the palladium content in Pt–Pd/alumina catalyst increased the oxidation activity and had more durability. While increasing the platinum content a little bit also improved the activity, adding much more did not. Supporting the platinum on alumina retarded the sintering of Pd and PdO, thus lengthening the oxidation activity of the Pt–Pd/alumina catalyst. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Pt/Pd-alumina; Methane oxidation; Natural gas engine exhaust; Lean burn; Durability; Sintering

1. Introduction

Lean-burn natural-gas engines have higher thermal efficiency than stoichiometric engines. The exhaust gases from lean-burn natural-gas engines contain hydrocarbons consisting mostly of unburned methane. Oxidizing this methane at low temperatures, such as at 658 K, is difficult because its light-off temperature is higher than that of other hydrocarbons. The traditional three-way catalyst used for controlling emissions from gasoline-powered vehicles is unable to oxidize all the hydrocarbons in lean-burn natural gas engine exhaust [1]. While there is much in literature concerning methane oxidation in near stoichiometric environments [1–5], very little published work is available for lean-burn natural-gas engine exhaust which contains 5% excess oxygen [6–11]. Most of these studies examined the effects of one-component noble metal supported on alumina [6–9]. Early work by McCormick et al. [10] demonstrates that low loading platinum and palladium supported on an alumina indicates rapid deactivation of hydrocarbon oxidation activity in lean-burn natural-gas engine exhaust. However, we have also observed very rapid activity loss for hydrocarbon conversion over low loading Pt–Pd/alumina, in high loading Pt–Pd/alumina it showed very high hydrocarbon oxidation activity and durability.

We have been studying and developing new catalysts for oxidizing methane at low temperatures in an attempt to find a better way to remove methane from lean-burn natural-gas engine exhaust [11]. In this paper, we report on the use of high loading Pt–Pd/alumina catalysts for oxidizing hydrocarbons in lean-burn natural-gas engine exhaust at low temperatures. We discuss the effect of metal loading on the Pt–Pd/alumina catalyst on the decrease in oxidation activity over time as a function of platinum and palladium

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contents, and compare its behavior with that for Pd/alumina and Pt/alumina under similar experimental conditions. Finally, we discuss the effect of platinum on the durability in the Pt–Pd/alumina catalyst.

2. Experimental

The catalysts were prepared by impregnation of an alumina-washcoating monolithic substrate (cordielite honeycomb) with 200 cells/in.^{2}. Precious metal and alumina support loadings for the volume of the monolith catalysts were given in g/l. Alumina loadings were 200 g/l. The alumina support had a surface area of 100 m^2/g.

The catalytic oxidation of hydrocarbons in lean-burn natural-gas engine (15 kW) exhaust was carried out in a conventional fixed-bed flow reactor with reaction tube 20 mm (inside) in diameter. The typical reaction conditions were as follows. The catalyst inlet temperature was 658 K (or 673 K, in Fig. 1). The gas hourly space velocity (GHSV) was 40 000 h^{-1}. The GHSV was calculated from the geometric catalyst monolith volume (multiplied cross-sectional area by length). Typical lean-burn natural-gas engine exhaust contains 3000 ppm of hydrocarbons (carbon basis), 4.9% of O_2 (dry basis), about 14% of H_2O. We analyzed the total amount of hydrocarbons (carbon basis) by using a hydrogen flame ionization detector (Horiba FIA-510 analyzer). The catalytic oxidation of methane in model gas was carried out in a conventional fixed-bed flow reactor with a catalyst inlet temperature of 658 K. The GHSV was 40 000 h^{-1}. The model gas mixture contained 2000 ppm of methane, 10.5% of O_2 (wet basis), and 10% of H_2O.

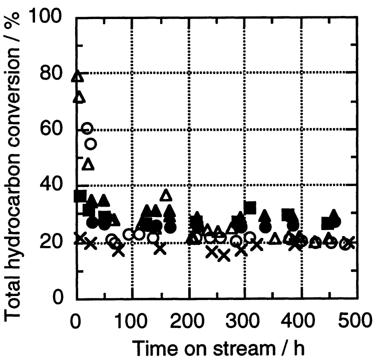

Fig. 1. Conversion of hydrocarbon at 673 K as a function of time on stream for various catalysts. (●) Pt(5 g/l)/alumina, (■) Pt(10 g/l)/alumina, (▲) Pt(20 g/l)/alumina, (○) Pd(10 g/l)/alumina, (△) Pd(50 g/l)/alumina, (×) Pt(1 g/l)–Rh(0.1 g/l)/alumina.

Table 1
Metal content in catalysts

Catalyst	Metal content[a] (g/l)	
	Pt	Pd
Pd(10 g/l)/alumina	0.0	10.4
Pd(50 g/l)/alumina	0.0	51.8
Pt(5 g/l)/alumina	(5)[b]	0.0
Pt(10 g/l)/alumina	9.6	0.0
Pt(20 g/l)/alumina	(20)[b]	0.0
Pt(10 g/l)–Pd(1 g/l)/alumina	9.6	1.3
Pt(10 g/l)–Pd(5 g/l)/alumina	9.6	5.0
Pt(10 g/l)–Pd(8 g/l)/alumina	9.6	9.6
Pt(10 g/l)–Pd(10 g/l)/alumina	10.4	10.4
Pt(10 g/l)–Pd(15 g/l)/alumina	9.6	18.3
Pt(15 g/l)–Pd(10 g/l)/alumina	14.3	11.9
Pt(8 g/l)–Pd(10 g/l)/alumina	7.9	11.1
Pt(5 g/l)–Pd(10 g/l)/alumina	5.5	11.1
Pt(1 g/l)–Pd(10 g/l)/alumina	2.2	11.1
Pt(0.1 g/l)–Pd(10 g/l)/alumina	0.2	11.9

[a] Content of metal was measured by ICP (inductively coupled plasma-optical emission analytical spectrometry).
[b] Parenthesis means loading ratio at preparation.

The performance of Pt–Rh/alumina catalyst (conventional three-way catalyst), Pd/alumina catalysts, Pt/alumina catalysts, and Pt–Pd/alumina catalysts were investigated in gas engine exhaust. The details of these catalysts are shown in Table 1.

The X-ray diffraction (XRD) analysis was done with a Phillips PW3020 diffractometer operating at 40 kV and 40 mA using Cu K_α radiation combined with a nickel filter. Crystallite sizes are estimated using the Scherrer equation from the peak width at half height of the Pd(1 1 1) and PdO(1 0 1) reflection.

3. Results and discussion

As shown in Fig. 1, the Pt(1 g/l)–Rh(0.1 g/l)/alumina and Pt/alumina catalysts had a low level of oxidation activity at 673 K, and the level remained fairly stable over the entire 500 h. The three Pt/alumina catalysts, which had platinum contents of 5–20 g/l, showed similar trends over the whole test period. The two Pd/alumina catalysts, which had

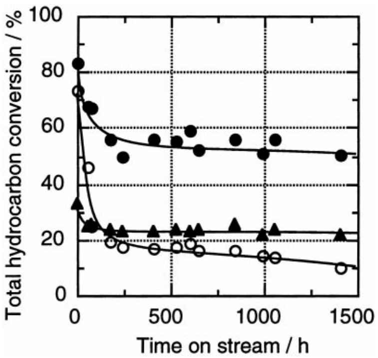

Fig. 2. Conversion of hydrocarbon at 658 K as a function of time on stream for various catalysts. (●) Pt(10 g/l)–Pd(10 g/l)/alumina, (▲) Pt(10 g/l)/alumina, (○) Pd(10 g/l)/alumina.

palladium contents of 10–50 g/l, both had a high initial activity. However, the activity quickly dropped and remained low for the rest of the test period. Therefore, increasing only the platinum or only the palladium content in each catalyst will neither increase nor lengthen the oxidation activity.

As shown in Fig. 2, the trend of the Pt(10 g/l)–Pd(10 g/l)/alumina catalyst is comparable to that of the Pt(10 g/l)/alumina and Pd(10 g/l)/alumina catalysts. The Pt–Pd/alumina catalyst showed the highest oxidation activity for the entire 1500 h test period. The activity of the Pt–Pd/alumina catalyst was very high initially, then dropped to about 50%. This high activity level is due to the high methane oxidation activity of the palladium. It stayed at a relatively high level due to the high stability of the platinum.

We investigated the effects of Pt and Pd loading on the performance of Pt–Pd/alumina catalysts by conducting a durability test using natural-gas engine exhaust. These durability tests were carried out at 658 K for 400 h. Afterwards, the oxidation activities of each catalyst were estimated and compared. As shown in Fig. 3, the total hydrocarbon oxidation activity increased with the platinum content up to 7 g/l, then remained constant up to about 15 g/l. This indicates that a platinum content level above about 7 g/l is not needed for this catalyst. As shown in Fig. 4, the total hydrocarbon oxidation activity increased with the palladium content up to 15 g/l.

The Pt(10 g/l)–Pd(15 g/l)/alumina catalyst exhibited the highest oxidation activity over the entire test period of the tested catalysts. As shown in Fig. 5, its oxidation activity remained at about 50% for about 2500 h.

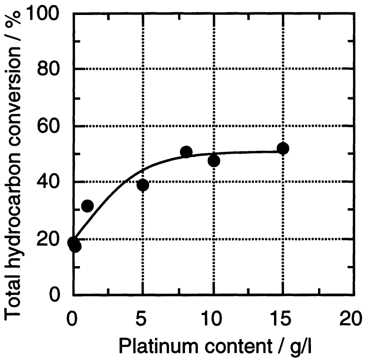

Fig. 3. Effect of Pt content on Pt–Pd/alumina. Conversion of hydrocarbon at 658 K after durability test for 400 h as a function of platinum content on Pt–Pd/alumina catalyst. Palladium content was constant at 10 g/l.

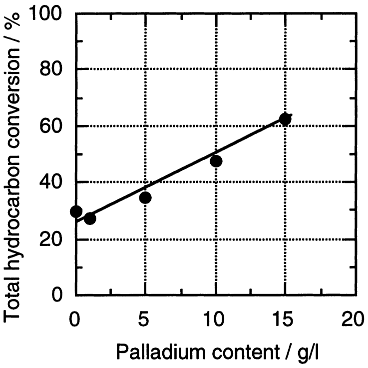

Fig. 4. Effect of Pd content on Pt–Pd/alumina. Conversion of hydrocarbon at 658 K after durability test for 400 h as a function of palladium content on Pt–Pd/alumina catalyst. Plantinum content was constant at 10 g/l.

A catalyst can be deactivated if its surface becomes covered with carbon. We investigated the effect of carbon deposition on the surfaces of Pd(50 g/l)/alumina and Pt(10 g/l)–Pd(10 g/l)/alumina catalysts by conducting an aging test at 658 K for 50 h in lean-burn natural-gas engine exhaust. The catalysts were then calcined at 823 K for 3 h under normal air conditions. The activities of their methane oxidations were evaluated by using a model gas containing excess oxygen. As shown in Table 2, before aging, both catalysts had high conversion levels. After aging, the activities of

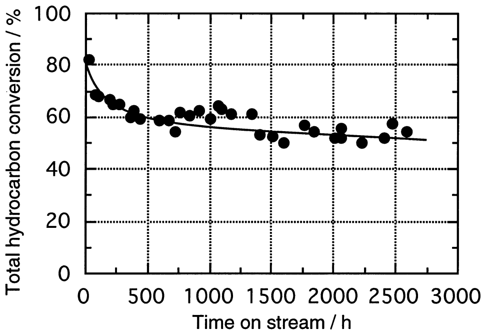

Fig. 5. Conversion of hydrocarbons at 658 K as a function of time on stream for Pt(10 g/l)–Pd(15 g/l)/alumina catalyst.

Table 2
Effect of carbon deposition[a]

Catalyst	Methane conversion (%)		
	Fresh	After aging test[b]	After calcination[c]
Pd(50 g/l)/alumina	77.0	25.4	25.1
Pt(10 g/l)–Pd(10 g/l)/alumina	79.0	59.0	55.7

[a] Catalytic activity measurement was carried out at 658 K and at GHSV of 40 000 h^{-1} under model gas.

[b] The aging test was carried out at 658 K for 50 h by using lean-burning natural-gas engine exhaust.

[c] The catalyst which was used at aging test was calcined at 823 K for 3 h.

both decreased, with that of the Pd/alumina catalyst decreasing much more than that of the Pt–Pd/alumina catalyst. The activities remained about the same after calcination at 823 K. This indicates that the carbon deposition does not affect the activities of either Pd/alumina or Pt–Pd/alumina catalysts. Therefore, the reduced activity of the Pd/alumina catalyst was not caused by carbon deposition.

We characterized the Pd/alumina and Pt–Pd/alumina catalysts by using XRD and transmission electron microscopy (TEM). The activities of these catalysts were found to be reduced by sintering of the Pd or PdO. Fig. 6 shows the growth of Pd crystallite size calculated from Pd(1 1 1) reflection with the aging time for Pd/alumina and Pt–Pd/alumina catalysts. Crystallite sizes were determined by measuring XRD patterns. The sintering rate of Pd(metal) in Pd/alumina catalyst remained fairly constant regardless of the Pd content and was faster than that of the Pd in the Pt–Pd/alumina catalyst. As shown in Fig. 7, the same tendency was found for PdO crystallite sizes estimated from PdO(1 0 1) reflection. These results suggest that the Pt supported on alumina retards the sintering of Pd and PdO crystallites. The same behavior was revealed by the TEM. After the aging test, the size of the Pd or PdO crystallites in the Pd/alumina catalyst was found to be larger than that of those in the Pt–Pd/alumina catalyst.

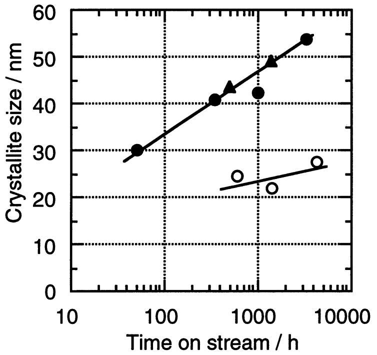

Fig. 6. Growth of Pd crystallite sizes calculated from Pd(1 1 1) reflection as a function of time on stream for various catalysts. (○) Pt(10 g/l)–Pd(10 g/l)/alumina, (▲) Pd(10 g/l)/alumina, (●) Pd(50 g/l)/alumina.

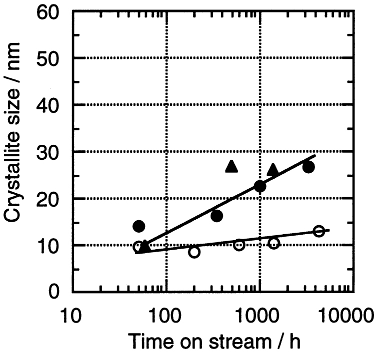

Fig. 7. Growth of PdO crystallite sizes calculated from PdO(1 0 1) reflection as a function of time on stream for various catalysts. (○) Pt(10 g/l)–Pd(10 g/l)/alumina, (▲) Pd(10 g/l)/alumina, (●) Pd(50 g/l)/alumina.

4. Conclusion

The Pt(10 g/l)–Pd(15 g/l)/alumina catalyst has a high hydrocarbon oxidation activity that remains fairly high during long usage in lean-burn natural-gas engine exhaust at low temperatures. The activity was still about 50% at 658 K after 2500 h. Platinum supported on alumina was found to retard the sintering of Pd and PdO crystallites. This slow sintering slows the decrease in activity of Pt–Pd/alumina catalyst.

References

[1] R.M. Siewart, P.J. Mitchell, European Patent 0 468 556 A1 (1991).
[2] T. Tabata, K. Baba, H. Kawashima, Appl. Catal. B 7 (1995) 19.
[3] S.H. Oh, P.J. Mitchell , R.M. Siewert, J. Catal. 132 (1991) 287.
[4] S.H. Oh, P.J. Mitchell, Appl. Catal. B 5 (1994) 165.
[5] R. Burch, F.J. Urbano, P.K. Loader, Proceedings of the First World Congress Environmental Catalysis, Pisa, 1995, p. 159.
[6] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 280.
[7] J.K. Lampert, R.J. Farrauto, E.M. Waterman, Proceedings of the First World Congress Environmental Catalysis, Pisa, 1995, p. 69.
[8] J.K. Lampert, M.S. Kazi, R.J. Farrauto, Appl. Catal. B 14 (1997) 211.
[9] J.K. Lampert, M.S. Kazi, R.J. Farrauto, SAE 96 1971 (1996).
[10] R.L. McCormick, A.W. Newlin, D. Mowery, M.S. Graboski, T.R. Ohno, SAE 96 1976 (1996).
[11] H. Uchida, F. Takashima, Y. Imaseki, Science and Technology in Catalysis 1994, Kodansha, Tokyo, 1995, p. 383.