Combustion of a trace amount of CH_4 in the presence of water vapor over ZrO_2-supported Pd catalysts

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Combustion of a trace amount of CH_4 over Pd catalysts supported on calcined ZrO_2 was examined under nearly exhaust gas conditions where the temperature is not so high and water vapor coexists. High catalytic activity was obtained with ZrO_2 support calcined at 1073 and 1273 K. The durability test at 673 K for 100 h revealed that the activity of these catalysts hardly decreased, while that of the Pd catalysts supported on calcined Al_2O_3 were much decreased in the course of time. These results demonstrated the advantages of ZrO_2 as a support for Pd catalysts in the present reaction.

Keywords: combustion, methane, palladium catalyst, zirconia, water vapor

1. Introduction

It is of progressively greater importance to remove catalytically a trace amount of hydrocarbons, especially CH_4, from exhaust gas of various kinds of engines, because CH_4 is 21 times more effective than CO_2 as a greenhouse gas [1]. As to the combustion of diluted CH_4, several efforts have so far been made on Pd catalysts supported on various materials, such as Al_2O_3 [2–4], mordenite [5,6], ZSM-5 [5,6] and silicoaluminophosphate-5 [7]. However, these Pd catalysts are not so effective from a practical point of view, since it is difficult to oxidize CH_4 completely under the exhaust gas conditions where the temperature is not so high and water vapor coexists. Thus, it is awaited to examine other materials as a support to develop effective Pd catalysts for the combustion of diluted CH_4 under such conditions.

Recently, the preparation of ZrO_2 with a large surface area has become possible [8–10], and there is now growing interest in using ZrO_2 as a support for environmental catalysts [11–15]. For example, Burch et al. examined Rh catalysts supported on heat-treated ZrO_2 and Al_2O_3, and found that ZrO_2 was superior to Al_2O_3 in the case of combustion of CH_4, although it was not the case for selective reduction of NO [11]. However, not so much is known on the properties of ZrO_2-supported catalysts under the above-mentioned exhaust gas conditions.

In the present study, the combustion of diluted CH_4 over Pd catalysts supported on calcined ZrO_2 was examined under nearly exhaust gas conditions, i.e., at lower temperatures in the presence of 10% water vapor together with CO_2 and CO. From a practical point of view, the activity of the examined catalysts toward the CH_4 combustion was compared on a per gram basis, and the durability was evaluated under the above conditions.

2. Experimental

The catalysts examined in the present study are listed in table 1. ZrO_2 (RC-100 obtained from Daiichi Kigenso Kagaku Kogyo Co., Ltd.) and Al_2O_3 (JRC-ALO-1 obtained from the Committee on Reference Catalysts of the Catalysis Society of Japan [16,17]) were calcined prior to introducing Pd to give the pre-specified surface areas. In the text, tables, and figures of the present paper, these support materials are abbreviated as $ZrO_2(873, 6)$, for example, which represents ZrO_2 calcined at 873 K for 6 h. The catalysts were prepared by an impregnation method using an aqueous solution of $Pd(NH_3)_4(OH)_2$ (obtained from Tanaka Kikinzoku Kogyo Co., Ltd.) followed by drying at 383 K for 12 h, reducing at 573 K for 3 h in a hydrogen gas flow, and calcining at 873 K for 6 h in an oxygen gas flow. Crystal phase of support, Pd loading and surface area were determined

Table 1
List of catalysts.

Catalyst symbol[a]	Crystal phase of support	Catalyst		
		Pd loading (wt%)	Pd dispersion (%)	Surface area ($m^2\,g^{-1}$)
$Pd/ZrO_2(873, 6)$	monoclinic	0.92	61.0	37.6
$Pd/ZrO_2(1073, 6)$	monoclinic	0.88	26.5	20.4
$Pd/ZrO_2(1273, 6)$	monoclinic	0.88	15.4	9.7
$Pd/ZrO_2(1473, 6)$	monoclinic	0.90	10.8	3.0
$Pd/Al_2O_3(1273, 6)$	α	0.88	34.7	69.9
$Pd/Al_2O_3(1273, 48)$	α	0.86	14.2	20.2

[a] For example, $Pd/ZrO_2(873, 6)$ stands for the Pd catalyst supported on ZrO_2 calcined at 873 K for 6 h.

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by X-ray powder diffraction, inductively coupled plasma atomic emission spectroscopy and the BET method using N_2 adsorption, respectively. Pd dispersion was estimated by the standard CO-pulse method as recommended by the Catalysis Society of Japan [18].

The catalytic test was carried out with a conventional continuous-flow reactor at atmospheric pressure, using catalysts in the form of 16–60 mesh granules. The catalyst (0.1 g unless otherwise noted) was dispersed in fused silica grains (0.2 g) to prevent scattering, and packed in a quartz tube of an inside diameter of 10 mm. Another quartz tube with an outside diameter of 6 mm, which makes a sheath for a thermocouple, was fitted to the center of the quartz tube of the catalyst column. Before the test, the packed catalyst was calcined at 873 K for 2 h in an air flow. After cooling it to the reaction temperature, the gas consisting of CH_4 (4000 ppm), CO (500 ppm), CO_2 (5%), O_2 (10%), H_2O (10%) and N_2 (balance) was fed at a space rate of 5000 $\mathrm{ml\,h^{-1}}$. Analysis of the produced gas was performed with a gas chromatograph, where the CO was oxidized completely under the examined conditions, as we confirmed separately.

The temperature-programmed desorption (TPD) experiment for ZrO_2 and Al_2O_3 was conducted using a conventional apparatus. After the calcination at 873 K for 2 h in an air flow, the powdery sample (250 mg) was exposed to 4.6 mmHg of H_2O at 673 K for 1 h in a He flow (100 $\mathrm{ml\,min^{-1}}$), followed by purging with a He flow (100 $\mathrm{ml\,min^{-1}}$) at the same temperature for 1 h. Then, the desorption of H_2O was measured on mass number 18 by a Q-Mass detector from 673 to 1073 K at a heating rate of 5 $\mathrm{K\,min^{-1}}$ under a He flow (100 $\mathrm{ml\,min^{-1}}$).

3. Results and discussion

The characterization results are summarized in table 1. The calcined ZrO_2 and Al_2O_3 samples were monoclinic and α phase, respectively. The Pd loading was around 0.9 wt%, not so much different from catalyst to catalyst. The surface area of Pd/ZrO_2, essentially equal to that of the calcined ZrO_2, decreased with increasing calcination temperature of the support oxide, and similarly that of Pd/Al_2O_3 decreased with increasing calcination time. The Pd dispersion tended to be lowered with decreasing surface area. However, the Pd dispersion on $ZrO_2(1073, 6)$ was higher than that on $Al_2O_3(1273, 48)$, although the surface area of $Pd/ZrO_2(1073, 6)$ was almost the same as that of $Pd/Al_2O_3(1273, 48)$.

Figure 1(a) shows the CH_4 conversion over the Pd/ZrO_2 catalysts as a function of reaction temperature in the absence of water vapor. The catalytic activity strongly depended on the calcination temperature of ZrO_2; the activity decreased in the order of $Pd/ZrO_2(1273, 6)$, Pd/ZrO_2 $(1073, 6)$, $Pd/ZrO_2(873, 6)$ and $Pd/ZrO_2(1473, 6)$. Among the catalysts $Pd/ZrO_2(1273, 6)$, $Pd/ZrO_2(1073, 6)$ and $Pd/ZrO_2(873, 6)$, the activity increased as the surface area and Pd dispersion decreased, as shown in table 1. Similar results have been reported, in which small Pd particles were found to be less active for CH_4 combustion than large ones [19,20]. The activity of the $Pd/ZrO_2(1473, 6)$ catalyst was extremely low, probably due to excessive sintering of ZrO_2. On the other hand, figure 1(b) shows the results of similar catalytic runs in the presence of 10% water vapor. As can be seen from figure 1 (a) and (b), the CH_4 conversion was significantly decreased by the presence of water vapor on all the catalysts examined. The decrease in conversion was not so much different from catalyst to catalyst, showing that water vapor inhibited the reaction over the Pd/ZrO_2 catalysts independently of the calcination temperature of ZrO_2. Such a depression caused by water vapor is probably due to the formation of inactive $Pd(OH)_2$ species on the active PdO surface, as suggested by Cullis et al. [21].

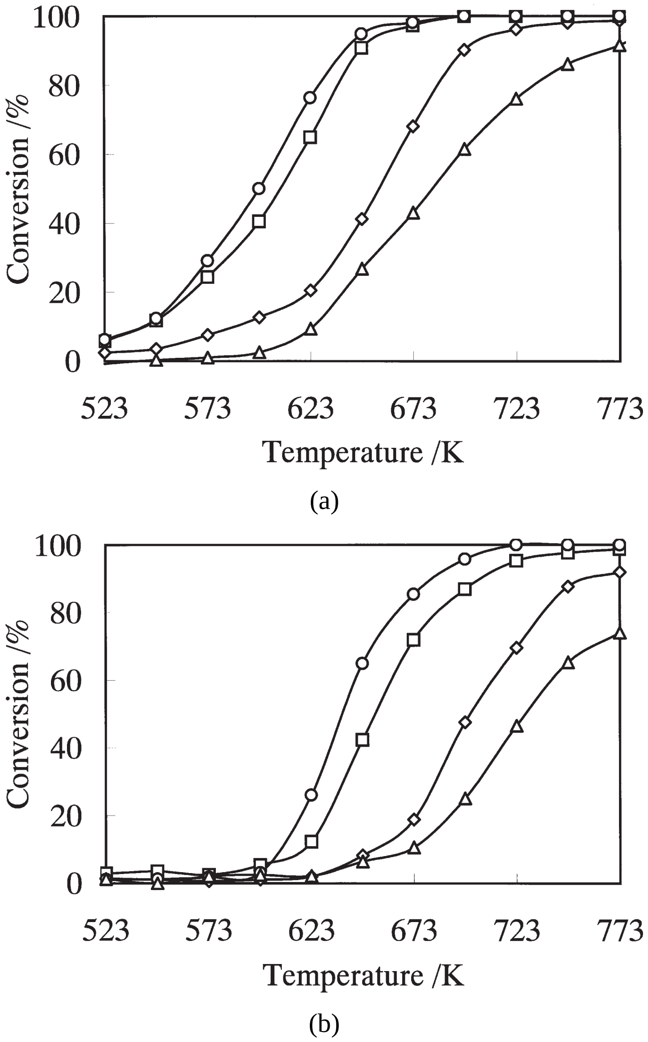

Figure 1. (a) CH_4 conversion in the absence of water vapor as a function of temperature. (b) CH_4 conversion in the presence of water vapor as a function of temperature. (◇) $Pd/ZrO_2(873, 6)$; (□) $Pd/ZrO_2(1073, 6)$; (○) $Pd/ZrO_2(1273, 6)$; (△) $Pd/ZrO_2(1473, 6)$.

From a practical point of view, we next examined the durability of the highly active catalysts, $Pd/ZrO_2(1073, 6)$ and $Pd/ZrO_2(1273, 6)$, at 673 K in the presence of water va-

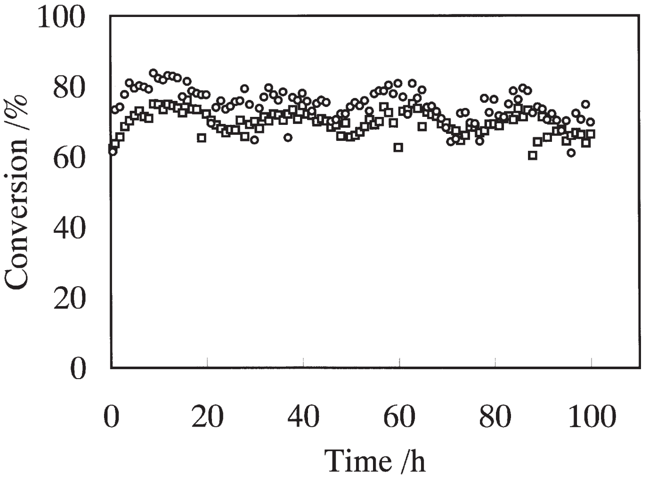

Figure 2. Time dependence in CH_4 conversion at 673 K in the presence of water vapor. (□) $Pd/ZrO_2(1073, 6)$; (○) $Pd/ZrO_2(1273, 6)$.

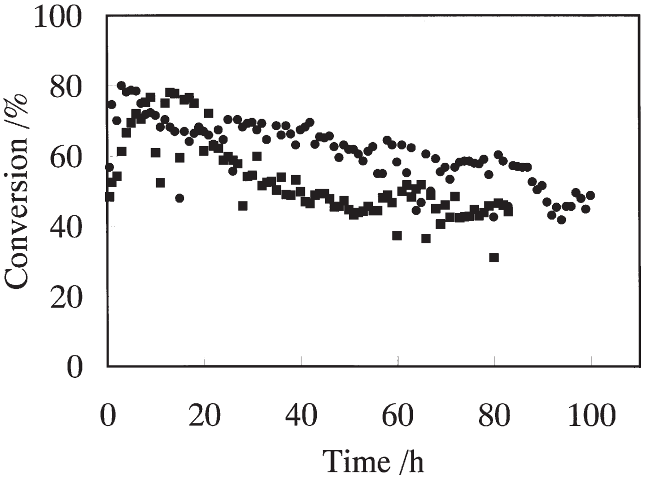

Figure 3. Time dependence in CH_4 conversion at 673 K in the presence of water vapor. (●) $Pd/Al_2O_3(1273, 48)$; (■) $Pd/Al_2O_3(1273, 6)$ (0.2 g).

por. As shown in figure 2, the CH_4 conversion was uneven against time, however, on the average, the initial conversion was kept up even after 100 h. In other words, any further deactivation was hardly caused, while water vapor significantly inhibited the reaction, as shown in figure 1.

For comparison, the same examination was carried out on the $Pd/Al_2O_3(1273, 48)$ catalyst, the surface area of which was almost the same as that of the $Pd/ZrO_2(1073, 6)$ catalyst. As shown in figure 3, the CH_4 conversion was as high as those over the $Pd/ZrO_2(1073, 6)$ and Pd/ZrO_2 $(1273, 6)$ catalysts at the initial stage of the test. After that, however, it gradually decreased with time and fell below 50% at the final stage. A similar test without water vapor revealed that the average CH_4 conversions over this catalyst (0.05 g) for 1–10 h and 91–100 h were 93 and 86%, respectively, suggesting that the lower durability in the presence of water vapor would be caused by the coexistent water vapor.

Furthermore, we examined the durability of the Pd/Al_2O_3 $(1273, 6)$ catalyst, the Al_2O_3 of which was heat-treated under the same conditions as the ZrO_2 of the $Pd/ZrO_2(1273, 6)$ catalyst. In this case, 0.2 g of catalyst was used because of its low activity. As shown in figure 3, the CH_4 conversion apparently increased for the initial 10 h, possibly due to increase in Pd particle size [22,23]. After that, however, the catalytic activity gradually decreased with time, as in the case of the $Pd/Al_2O_3(1273, 48)$ catalyst. These examinations show that water vapor brought about the gradual decrease in activity of the Pd/Al_2O_3 catalysts with time, independently of the heat-treatment conditions for Al_2O_3.

Table 2
Pd dispersion and surface area before and after durability test.

Catalyst symbol	Pd dispersion (%)		Surface area ($m^2\,g^{-1}$)	
	Before	After	Before	After
$Pd/ZrO_2(1073, 6)$	26.5	16.4	20.4	21.4
$Pd/ZrO_2(1273, 6)$	15.4	12.7	9.7	8.1
$Pd/Al_2O_3(1273, 6)$	34.7	23.3	69.9	60.3
$Pd/Al_2O_3(1273, 48)$	14.2	7.4	20.2	21.6

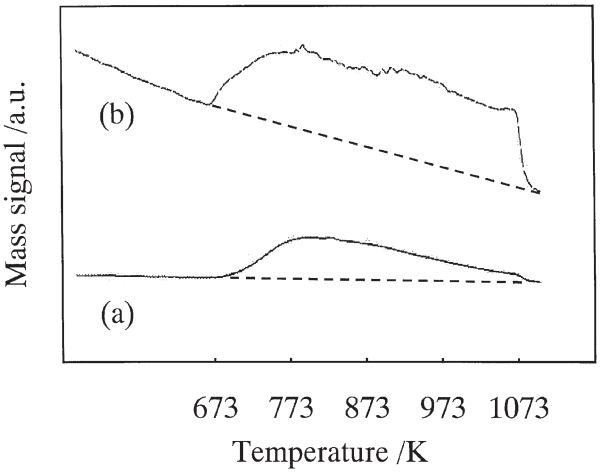

Figure 4. H_2O-TPD profiles of ZrO_2 and Al_2O_3. (a) $ZrO_2(1073, 6)$; (b) $Al_2O_3(1273, 48)$.

Table 2 summarizes the Pd dispersion and surface area of the catalysts before and after the durability test. The surface area was not so much changed after the test. On the other hand, the Pd dispersion was decreased on all the catalysts examined, however, lower Pd dispersion did not necessarily result in lower CH_4 conversion, as shown earlier. Indeed, it has also been reported that small dispersed Pd particles are less active than large ones [19,20]. Thus, we could not explain the difference in durability between the two kinds of catalysts in the aspect of Pd surface area.

In order to explain the reasons for the higher durability of Pd/ZrO_2, it is next necessary to compare the hydrophobicity of ZrO_2 with that of Al_2O_3 under the reaction temperature. Figure 4 shows the H_2O-TPD profiles on $ZrO_2(1073, 6)$ (surface area is 20.4 $m^2\,g^{-1}$) and Al_2O_3 $(1273, 48)$ (20.2 $m^2\,g^{-1}$) from 673 to 1073 K. In the case of $ZrO_2(1073, 6)$, the desorption was nearly completed up to 1073 K, while, in the case of $Al_2O_3(1273, 48)$, it was likely to continue after the measurement was ceased at 1073 K.

However, according to the profiles, the amounts of desorbed H_2O on $ZrO_2(1073, 6)$ and $Al_2O_3(1273, 48)$ were calibrated to be 0.011 and 0.031 $\mathrm{mmol\,g^{-1}}$, respectively, showing the relative hydrophobicity of ZrO_2 compared to Al_2O_3. On the basis of this finding, although the details are not yet known, the higher durability of Pd/ZrO_2 would be resulted from the relative hydrophobicity of ZrO_2 to restrain morphological changes in Pd particles, such as the formation of inactive $Pd(OH)_2$ species, in the course of time.

In conclusion, Pd catalysts supported on moderately calcined ZrO_2 were shown to be promising for combustion of a trace amount of CH_4 in exhaust gas: The Pd/ZrO_2 catalysts exhibit as high an initial activity as a Pd catalyst supported on calcined Al_2O_3, and further, they exhibit a higher durability than the Pd/Al_2O_3 catalyst at a low temperature in the presence of water vapor.

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References

[1] E.S. Rubin, R.N. Cooper, R.A. Frosch, T.H. Lee, G. Marland, A.H. Rosenfield and D.D. Stine, Science 257 (1992) 148.
[2] R. Burch, F.J. Urbano and P.K. Loader, Appl. Catal. A 123 (1995) 173.
[3] R. Burch and P.K. Loader, Appl. Catal. B 5 (1995) 149.
[4] R.G. Silver and J.C. Summerts, Stud. Surf. Sci. Catal. 96 (1995) 871.
[5] Y. Li and J.N. Armor, Appl. Catal. B 3 (1994) 275.
[6] C.M. de Correa and A.L. Villa H., Appl. Catal. B 10 (1996) 313.
[7] K. Nomura, K. Noro, Y. Nakamura, Y. Yazawa, H. Yoshida, A. Satsuma and T. Hattori, Catal. Lett. 53 (1998) 167.
[8] M. Inoue, H. Kominami and T. Inui, Appl. Catal. A 121 (1995) L1.
[9] M. Inoue, H. Kominami and T. Inui, Appl. Catal. A 97 (1993) L25.
[10] J.C. Duchet, M.J. Tilliette and D. Cornet, Catal. Today 10 (1991) 507.
[11] R. Burch and P.K. Loader, Appl. Catal. A 143 (1996) 317.
[12] G. Pecchi, P. Reyes, R. Gómez, T. López and J.L.G. Fierro, Appl. Catal. B 17 (1995) L7.
[13] M. Marella, M. Tomaselli, L. Meregalli, M. Battagliarin, P. Gerontopoulos, F. Pinna, M. Signoretto and G. Strukul, in: *Scientific Bases for the Preparation of Heterogeneous Catalysts*, eds. G. Poncelet et al. (Elsevier, New York, 1995) p. 323.
[14] K. Fujimoto, F.H. Ribeiro, M. Avalos-Borja and E. Iglesia, J. Catal. 179 (1998) 431.
[15] J.N. Carstens, S.C. Su and A.T. Bell, J. Catal. 176 (1998) 136.
[16] Y. Murakami, Stud. Surf. Sci. Catal. 16 (1983) 775.
[17] T. Uchijima, in: *Catalytic Science and Technology*, Vol. 1, eds. S. Yoshida, N. Takezawa and T. Ono (Kodansha, Tokyo, 1991) p. 393.
[18] T. Hattori, H. Matsumoto and Y. Murakami, Stud. Surf. Sci. Catal. 31 (1987) 815.
[19] R.J. Farrauto, M.C. Hobson, T. Kennelly and E.M. Waterman, Appl. Catal. A 81 (1992) 227.
[20] F.H. Ribeiro, M. Chow and R.A. Dalla Betta, J. Catal. 146 (1994) 537.
[21] C.F. Cullis, T.G. Nevell and D.L. Trimm, J. Chem. Soc. Faraday Trans. I 68 (1972) 1406.
[22] T.R. Baldwin and R. Burch, Catal. Lett. 6 (1990) 131.
[23] P. Briot and M. Primet, Appl. Catal. 68 (1990) 301.