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Catalytic activity of PdO/ZrO_2 catalyst for methane combustion

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Abstract

Catalytic activity of ZrO_2 supported PdO catalysts for methane combustion has been investigated in comparison with Al_2O_3 supported PdO catalysts. It was found that the drop of catalytic activity owing to decomposition of PdO at a high temperature region (600–900°C) was suppressed by using ZrO_2 support. Temperature-programmed reduction (TPR) measurements of the catalyst with hydrogen revealed that the PdO of PdO/Al_2O_3 catalyst was reduced at the temperature less than 100°C, whereas in PdO/ZrO_2 catalyst the consumption of hydrogen was also observed at 200–300°C. This result indicates that the stable PdO species were present in the PdO/ZrO_2 catalyst. In order to confirm the formation of the solid solution of PdO and ZrO_2, X-ray diffraction (XRD) analyses of the mixtures of ZrO_2 and PdO calcined at 700–900°C in air were carried out. The lattice volume of ZrO_2 in the mixture was larger than that of ZrO_2. Furthermore, the Pd thin film on ZrO_2 substrate was prepared as a model catalyst and the depth profile of the elements in the Pd thin film was measured by Auger electron spectroscopy (AES). It was confirmed that Zr and O as well as Pd were present in the Pd thin film heated at 900°C in air. It was considered that the PdO on ZrO_2 support might be stabilized by the formation of the solid solution of PdO and ZrO_2.

Keywords: Methane combustion; PdO/ZrO_2 catalysts; Temperature-programmed reduction; X-ray diffraction; Auger electron spectroscopy

1. Introduction

Catalytic combustion has many advantages compared with conventional flame combustion. Emission of NO_x can be greatly diminished because of low operating temperature and high energy efficiency can be obtained by stable combustion of lean fuels [1–3]. Supported palladium catalysts are widely well known to be active for methane combustion. However, one of major problem of this catalyst system is the decrease of the catalytic activity caused by the decomposition of the active component PdO into Pd metal at the high temperature [4–7]. Therefore, it is important to form the stable PdO species which hardly decompose even at the high temperature. Sekizawa et al. have reported that a drop of catalytic activity at the high temperature range could be avoided by use of Mn-substituted hexaaluminate as a catalyst support [5]. In this work, the effect of supports on the catalytic activity for methane combustion at a high temperature region (600–900°C) has been studied.

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2. Experimental

The supports used for the catalysts were ZrO_2 (Tosoh Corporation, TZ-0, BET surface area: 14.7 $m^2 g^{-1}$), ZrO_2-δ-Al_2O_3 (74.1 $m^2 g^{-1}$) and δ-Al_2O_3 (Showa Aluminum Industries, UA-5605, 77.4 $m^2 g^{-1}$). The 10 mol% ZrO_2-δ-Al_2O_3 support was prepared by impregnating δ-Al_2O_3 with an ethanol solution of $Zr(C_5H_7O_2)_4$, followed by drying and calcination at 1000°C for 2 h in air. Supported PdO catalysts were prepared by impregnating the supports with an ethanol solution of $Pd(C_5H_7O_2)_2$. After drying, the catalyst precursors were calcined at 500, 700, 900 and 1100°C for 4 h in air. The loading amount of Pd metal was 0.5 wt%.

The combustion reaction of CH_4 with air was carried out using a flow type fixed bed reactor under atmospheric pressure. The granulated catalysts of 0.6–1.2 mm in diameter and alumina beads were packed in the reactor. A gas mixture containing 0.5% of CH_4 in air was fed to catalyst bed at a space velocity of 50 000 h^{-1}. The reactor was heated by electric furnace. The reaction effluents after 14 min at the prescribed temperature were analyzed by on-line gas chromatography.

Temperature-programmed reduction (TPR) of PdO was carried out in a flow system (Altamira Instruments, AMI-1), in which the catalyst samples were heated up at a constant rate of 10°C min^{-1} in a 10% H_2-90% Ar stream (30 ml/min). The consumption of hydrogen was measured from the effluent gas by using a TCD cell and an on-line quadrupole mass spectrometer MMC-200 of Ulvac Japan.

The Pd dispersions of the catalysts were evaluated by measurement of CO adsorption in which, prior to CO adsorption measurement, samples were reduced at 120°C for 15 min in a hydrogen stream.

In order to confirm the formation of the solid solution of PdO and ZrO_2, the lattice volume of ZrO_2 was calculated from the lattice constants obtained from a Mac Science diffractometer using CuK_α radiation. The mixtures (molar ratio of PdO/ZrO_2=1) of ZrO_2 and PdO (Kojundo Chemical Laboratory, 17.1 $m^2 g^{-1}$) calcined at 700 and 900°C for 4 h in air were analyzed. Silicon was used as a standard specimen for the measurement of lattice constants.

Further the depth profile measurements of the Pd thin film on a ZrO_2 substrate as a model catalyst were carried out by Auger electron spectroscopy (AES) 670xi of PHI with an Ar ion gun. The model catalyst was prepared by a sputtering method. A Pd thin film of about 12 nm thick was formed on the polished ZrO_2 substrate. The model catalysts were calcined at 500, 700 and 900°C for 4 h in air. The etching rate by an Ar ion gun was 4 nm/min in the case sputtered SiO_2 film on Si substrate.

3. Results and discussion

The catalytic activities for methane combustion over supported PdO catalysts were measured as a function of temperature. The effect of supports on the catalytic activity is shown in Fig. 1, in which methane conversions are measured ones in cooling the reaction temperature down from 1000°C over supported PdO catalysts calcined at 1100°C for 4 h in air. Every catalyst showed the drop of methane conversion at a high temperature region (600–900°C) owing to decomposition of PdO. The drop of methane conversion at this temperature region was decreased in the following order: PdO/ZrO_2<PdO/ZrO_2-δ-Al_2O_3< PdO/δ-Al_2O_3.

Fig. 2 shows the effect of calcination temperature on the catalytic activity for methane combustion over PdO/ZrO_2 catalysts in the case of cooling down from

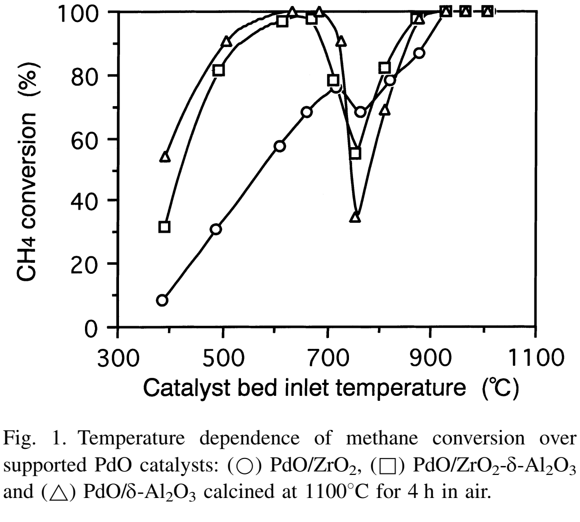

Fig. 1. Temperature dependence of methane conversion over supported PdO catalysts: (○) PdO/ZrO_2, (□) PdO/ZrO_2-δ-Al_2O_3 and (△) PdO/δ-Al_2O_3 calcined at 1100°C for 4 h in air.

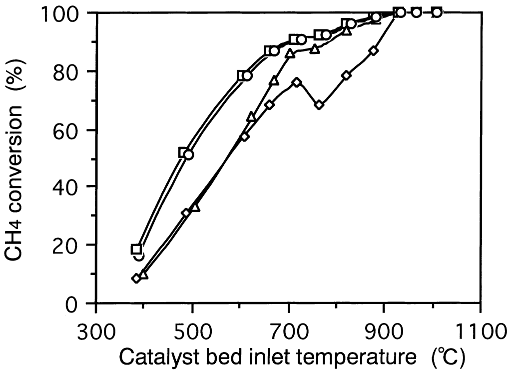

Fig. 2. Temperature dependence of methane conversion over PdO/ZrO_2 catalysts calcined at (○) 500°C, (□) 700°C, (△) 900°C and (◇) 1100°C for 4 h in air.

1000°C. The little drop of methane conversion was observed for the PdO/ZrO_2 catalysts calcined below 900°C. However, the drop of methane conversion was clearly observed when the PdO/ZrO_2 catalyst was calcined at 1100°C.

The TPR profiles over 100°C of supported PdO catalysts calcined at 500°C are shown in Fig. 3, since most parts of PdO of every catalyst was reduced at the temperature less than 100°C by the hydrogen. In the PdO/δ-Al_2O_3 catalyst, no peak was observed over 100°C. On the other hand, in the PdO/ZrO_2 and PdO/ZrO_2-δ-Al_2O_3 catalyst, the peak by the consumption of hydrogen was observed at 200–300°C. Asakura et al. have reported that the interface structure of the PdO/ZrO_2 was stable against the hydrogen reduction at 200°C [8]. Since no consumption of hydrogen was observed from TPR of supports, it was suggested that the stable PdO species were present on the PdO/ZrO_2 and PdO/ZrO_2-δ-Al_2O_3 catalyst. The stable PdO species might be formed in the PdO/ZrO_2 interface when the catalyst was calcined at 500°C. The amounts of hydrogen consumption at 200–300°C were calculated from TCD peak area (shade area in Fig. 3) and summarized in Table 1. There appeared to be correlation between the amount of hydrogen consumption and the drop of methane conversion at a high temperature region (600–900°C). It is considered that the PdO/ZrO_2 catalyst have high catalytic activity at a high temperature region because of the presence of stable PdO species on the catalyst support.

The amounts of hydrogen consumption at 200–300°C with PdO/ZrO_2 catalysts are shown in Table 2.

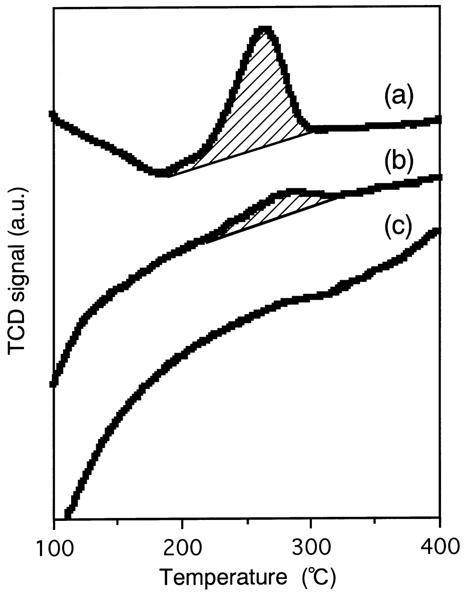

Fig. 3. TPR profiles of supported PdO catalysts: (a) PdO/ZrO_2, (b) PdO/ZrO_2-δ-Al_2O_3 and (c) PdO/δ-Al_2O_3 calcined at 500°C for 4 h in air.

Table 1
Amounts of hydrogen consumption at 200–300°C with supported catalysts

Catalysts[a]	Amount of hydrogen consumption at 200–300°C (μmol/g-catalyst)
PdO/ZrO_2	12.4
PdO/ZrO_2-δ-Al_2O_3	4.5
PdO/δ-Al_2O_3	0

[a]Calcined at 500°C for 4 h in air.

Table 2
Amounts of hydrogen consumption at 200–300°C with PdO/ZrO_2 catalysts

Calcination temperature	Amount of hydrogen consumption	
(°C)	(μmol/g-catalyst)[a]	(%)[b]
500	12.4	26
700	15.9	34
900	19.2	41
1100	7.2	15

[a]Calculated from TCD peak area.
[b]Percentages of reduced Pd to the loaded PdO.

Table 3
Surface areas and Pd dispersions with PdO/ZrO_2 catalysts

Calcination temperature (°C)	Surface area[a] ($m^2 g^{-1}$)	Pd dispersion[b] (CO/Pd)
500	15.0	0.32
700	14.0	0.31
900	11.8	0.29
1100	4.4	0.12

[a] BET method with N_2.
[b] Evaluated by CO adsorption.

It increased as calcination temperature of catalyst was raised. The catalyst calcined at 900°C showed the largest amount of hydrogen consumption among the catalysts and the value was 19.2 μmol/g-catalyst which corresponded to the reduction of 41% of the loaded PdO. This effect of the calcination temperature indicates that the stable PdO species could be formed by the solid reaction between PdO and ZrO_2. There was a significant decrease of the amount of hydrogen consumption at 200–300°C when the PdO/ZrO_2 catalyst was calcined at 1100°C. These results suggested that the amount of stable PdO species was correlated with the drop of methane conversion at a high temperature region.

The surface areas and the Pd dispersions with PdO/ZrO_2 catalysts are shown in Table 3. Both the surface area and the Pd dispersion decreased gradually as increasing calcination temperature below 900°C and showed a significant decrease at a calcination temperature of 1100°C. The particle growth of both the supported PdO and the ZrO_2 support by the calcination at too high temperature would lower the activity of the solid reaction, since the amounts of stable PdO species for the PdO/ZrO_2 catalyst calcined at 1100°C decreases significantly. Furthermore, it was considered that the calcination at the temperature above 900°C could be disadvantage to form the stable PdO species because the decomposition of PdO to Pd metal took place at such a high temperature.

The supported PdO on the support was observed by transmission electron microscopy (TEM). Fig. 4 shows the typical micrographs of PdO/ZrO_2 (a) and $PdO/\delta\text{-}Al_2O_3$ (b) catalyst calcined at 1100°C for 4 h in air. The calcination at 1100°C caused the significant growth of PdO particles on the $\delta\text{-}Al_2O_3$ support. The sizes of PdO particles on the $\delta\text{-}Al_2O_3$ support were larger than those of the $\delta\text{-}Al_2O_3$ support. On the other hand, the PdO particles on the ZrO_2 support were hardly observed. The sizes of PdO particles on the ZrO_2 support were much smaller than those of PdO on the $\delta\text{-}Al_2O_3$ support and the PdO adhering strongly to the surface of ZrO_2 support was observed as shown in Fig. 4(a). It is thought that the solid solution of PdO and ZrO_2 might be formed and hence the PdO on the ZrO_2 support could not be observed as the particles.

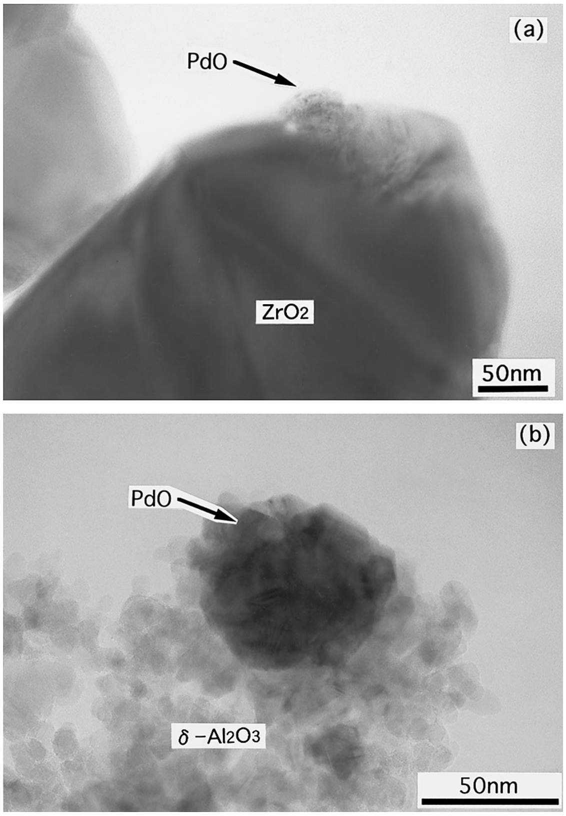

Fig. 4. TEM photographs of supported PdO catalysts: (a) PdO/ZrO_2 and (b) $PdO/\delta\text{-}Al_2O_3$ calcined at 1100°C for 4 h in air.

In order to confirm the formation of the solid solution of PdO and ZrO_2, XRD analyses of the mixtures of PdO and ZrO_2 calcined at 700 and 900°C for 4 h in air were carried out. All diffraction peaks were assigned to those for PdO and ZrO_2 and no diffraction peaks from the Zr–Pd–O compounds. The changes in the lattice volume of ZrO_2 calculated from the lattice constants are shown in Fig. 5. The lattice

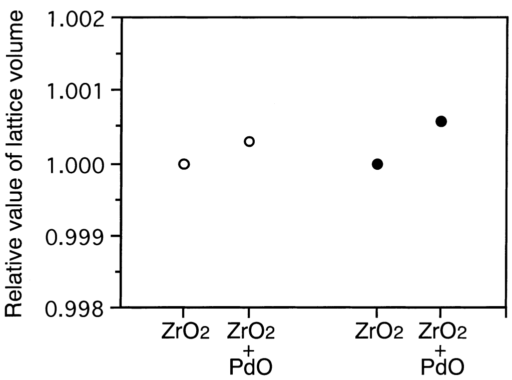

Fig. 5. Changes in the lattice volume of ZrO_2 in the mixture after calcination at (○) 700°C and (●) 900°C for 4 h in air.

volume of ZrO_2 in the mixture of ZrO_2 and PdO is the normalized value by the lattice volume of pure ZrO_2. The lattice volume of ZrO_2 in the mixtures calcined at 700 and 900°C was larger than that of ZrO_2. Since the ion radius of Pd^{2+} is slightly larger than that of Zr^{4+} [9], the lattice volume of ZrO_2 in the mixture should increase if the solid solution of PdO and ZrO_2 is formed. This is in good agreement with the changes in the lattice volume of ZrO_2.

The depth profiles of the elements in the model catalyst (Pd thin film/ZrO_2 substrate) by AES are shown in Fig. 6. The vertical axis of Fig. 6 is the percentages of atomic concentration normalized by the relative sensitivity factor of O, Zr and Pd, respectively. The abscissa is the etching time (min) which corresponds to the depth from the surface. The depth profiles of the model catalyst as prepared indicated that about 12 nm thickness of the Pd thin film was formed on the ZrO_2 substrate. The Pd films after heating at 500 and 700°C for 4 h in air were completely oxidized to the form of PdO. In cases of heating at 500 and 700°C, the transformations of

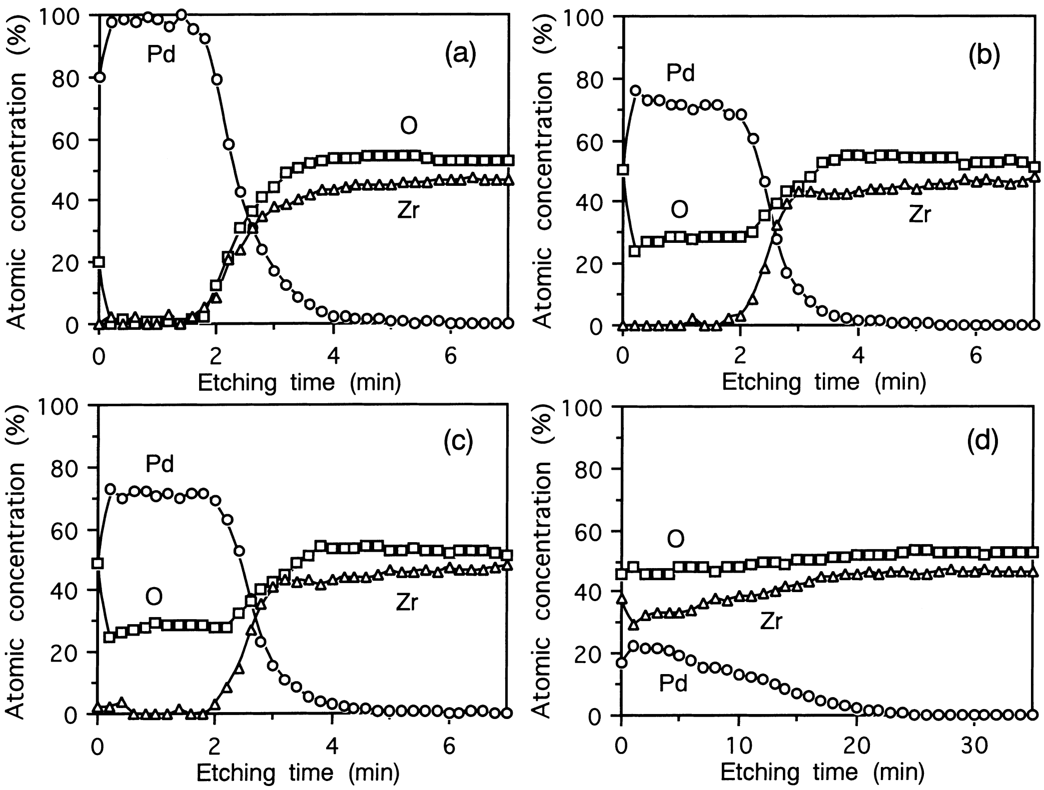

Fig. 6. AES depth profiles of the elements in the model catalyst (Pd thin film/ZrO_2 substrate): (a) as prepared calcined at (b) 500°C, (c) 700°C and (d) 900°C for 4 h in air.

PdO/ZrO_2 interface were not observed. After heating at 900°C for 4 h in air, Zr and O as well as Pd were detected from the Pd film layer in the model catalyst. The thickness of the layer consisted of Pd, Zr and O was to about five times of the thickness of Pd film layer as prepared. It was thought that the solid reaction between PdO and ZrO_2 could not take place in cases of heating at 500 and 700°C because the area of contact between PdO and ZrO_2 in this model catalyst was insufficient to form the solid solution.

4. Conclusion

It was found that the drop of catalytic activity owing to decomposition of PdO at a high temperature region (600–900°C) was suppressed by using ZrO_2 support. This result can be explained as the presence of stable PdO species in the PdO/ZrO_2 interface. It was considered that the PdO on ZrO_2 support might be stabilized by the formation of the solid solution of PdO and ZrO_2.

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