Acid Strength of Support Materials as a Factor Controlling Oxidation State of Palladium Catalyst for Propane Combustion

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The support effect on the low temperature catalytic combustion of propane over palladium catalyst was studied by using a series of metal oxides as support materials: MgO, ZrO_2, Al_2O_3, SiO_2, SiO_2–ZrO_2, SiO_2–Al_2O_3, and SO_4^{2-}–ZrO_2. The catalytic activity varied with the kind of the support materials; a support material with moderate acid strength gave maximum conversion. In order to discuss more details, 5 wt% Pd/ZrO_2, Pd/Al_2O_3, and Pd/SiO_2–Al_2O_3 were subjected to catalytic testing under the various conditions, and the catalysts after the test were characterized by XRD and XPS. The activity changed with the oxygen concentration, and the concentration providing the maximum activity depended on the support material. The maximum activity was obtained at high concentration on Pd/SiO_2–Al_2O_3, at moderate concentration on Pd/Al_2O_3, and at low concentration on Pd/ZrO_2. This sequence corresponded to that of acid strength of the support materials measured by Hammett indicators. The relation between the oxidation state of palladium and its catalytic activity under the various mixtures indicated that the catalytic activity on each catalyst depends on the oxidation state of palladium, and that partially oxidized palladium is effective for propane combustion. Moreover, palladium on acidic support kept the metallic state even under high oxygen concentration, indicating that acidic support gives palladium the resistibility against oxidation. These results suggest one guideline for the design of active palladium catalyst; an acidic support must be chosen under the mixture of the higher oxygen concentration and vice versa. © 1999 Academic Press

Key Words: acid strength of support materials; oxidation state of palladium; palladium; propane combustion; support effect.

1. INTRODUCTION

The catalytic combustion of hydrocarbons is an important technology for the production of energy (e.g., gas turbines) and for reducing the emission of pollutants (e.g.,

automotive exhausts). Palladium and platinum catalysts are the most active catalysts for the combustion (1, 2). In catalytic combustion of hydrocarbons over palladium catalysts, it has been widely accepted that supported palladium is oxidized during the reaction and that the catalytic activity of palladium catalysts changes with the oxidation state of palladium; it was suggested that partially oxidized palladium is most active in combustion of methane (3–5). In the case of propane combustion over Pd/SiO_2–Al_2O_3, the authors also clarified that the partially oxidized palladium is most active (6).

The property of supported precious metals is varied with the support materials in many catalytic reactions. It was reported that the stability of palladium oxide (7, 8) and the ability of palladium to adsorb oxygen (9) changed with the support. However, it is ambiguous what property of support material affects the property of supported palladium.

In propane combustion, Ishikawa *et al.* (10) showed that platinum on the support having stronger acid strength exhibited higher catalytic activity and suggested the possibility that acidic support materials prevent the oxidation of supported platinum. In the present paper, we investigated propane combustion over palladium catalysts supported on various oxides not only to elucidate the effect of the support material on the catalytic activity, but also to propose acid strength of support materials as a new parameter for the design of effective palladium catalyst.

2. EXPERIMENTAL

2.1. Catalysts Preparation

The catalysts employed were supported palladium on a series of metal oxides shown in Table 1. MgO, Al_2O_3, SiO_2, and SiO_2–Al_2O_3 are the reference catalysts of the Catalysis Society of Japan (JRC-MGO-1, ALO-4, SIO-8, and SAL-2) (11, 12). ZrO_2 was obtained by calcination of $Zr(OH)_4$ at 773 K for 3 h in air. $Zr(OH)_4$ was obtained by hydrolyzing $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonia followed

TABLE 1

The Property of a Series of Palladium Catalysts

Support	Surface area of support $(m^2 \, g^{-1})$	Acid strength of support (pKa)	Pd dispersion (%)
MgO[a]	138	22.3	21
ZrO$_2$	53	9.3	41
Al$_2$O$_3$[b]	183	3.3	34
SiO$_2$[c]	341	−5.6	9
SiO$_2$–ZrO$_2$[d]	210	−8.2	16
SiO$_2$–Al$_2$O$_3$[e]	543	−11.99	12
SO$_4^{2-}$–ZrO$_2$	111	−13.16	2[f]

[a] JRC-MGO-1 (JRC, Japan Reference Catalyst).
[b] JRC-ALO-4.
[c] JRC-SIO-8.
[d] Zr/Si = 0.4 by mol.
[e] JRC-SAL-2 (SiO$_2$–Al$_2$O$_3$ catalyst with 13 wt% Al$_2$O$_3$).
[f] The dispersion was ca. 10% by TEM measurement.

by washing and drying. SO$_4^{2-}$–ZrO$_2$ was obtained by immersing a fine powder of Zr(OH)$_4$ on a filter paper in 0.5 M H$_2$SO$_4$ followed by drying and calcining at 923 K for 3 h (13). SiO$_2$–ZrO$_2$ prepared by sol-mixing method was supplied from Nikki Chemicals Co. Ltd. All support materials thus obtained were sieved to +25–50 mesh. These support materials employed are stable under the reaction conditions.

Supported palladium catalysts were prepared by impregnating support materials with an acetone solution of Pd(CH$_3$COO)$_2$ followed by drying at 383 K for 12 h, calcining at 673 K for 3 h, and reducing at 623 K for 3 h in a flowing H$_2$. In order to observe the oxidation state of palladium particle by X-ray diffraction, the palladium loading was determined to be 5 wt% as palladium.

2.2. Propane Combustion

Catalytic runs were conducted by using a conventional flow reaction apparatus. A small amount of catalyst (0.01 g) was dispersed in 1.0 g of quartz granules to prevent a local increase of temperature and packed in a quartz reactor with an inside diameter of 10 mm. The thermocouple, sheathed by a quartz tube with an outside diameter of 6 mm, was fixed in the center of the catalyst bed. The reactor was installed in an electrically heated fluidized sand bath in order to heat the catalyst bed uniformly. Before the catalytic run, the catalyst was pretreated in a flow of N$_2$ + H$_2$ mixture (N$_2$/H$_2$ = 4) at 823 K for 2 h and then cooled to 473 K in flowing nitrogen. The concentration of propane in the reaction mixture was 0.25% and that of oxygen was changed from 1.25 to 9.0%. The reaction mixture will hereafter be represented by S value corresponding to the oxygen concentration relative to stoichiometric one, i.e., $S = [O_2]/5[C_3H_8]$. Nitrogen was used as a balance gas, and total flow rate was 200 ml min^{-1}.

This reaction condition was selected to avoid diffusional limitation.

The catalytic activity was examined as follows: the reaction temperature was raised stepwise every 50 K from 473 to 873 K. At each step, after the bed temperature attained the desired value, the reaction condition was kept for 25 min, and then the products were analyzed by gas chromatography. For the characterization of catalysts after the reaction, another catalytic run was conducted in the same way as above except that the run was interrupted at 773 K.

2.3. Characterization

The BET surface area of the support oxide was measured through N$_2$ adsorption at liquid nitrogen temperature by using a conventional flow-type adsorption apparatus. The acid strength of the support was measured through the changes in color of Hammett indicators adsorbed on the support that had been precalcined at 773 K for 3 h.

The dispersion of palladium of the reduced catalyst was measured through the pulse adsorption of CO in a flow of the carrier gas (He) (11, 12). The catalyst surface was cleaned up by heating in flowing oxygen at 573 K for 15 min, and then the catalyst was reduced in flowing hydrogen at 673 K for 30 min. For the analysis of the dispersion of palladium of the used catalyst, the catalyst was reduced for 1 h at 673 K. This reduction condition was confirmed to satisfy the requirements for reduction of supported palladium without changing the particle size (11, 12). The dispersion of palladium was calculated from the total CO uptake by assuming a stoichiometry of CO/Pd$_{surface}$ = 1.

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed for analysis of the oxidation state of palladium on the catalyst used for the reaction. XRD patterns were obtained by using RINT-1200 (Rigaku). Cu$K\alpha$ X-rays were used as the X-ray source. XPS spectra were obtained by using AXIS-HSi (Shimadzu). Monochromatized Al$K\alpha$ X-rays were used as the X-ray source. The oxidation state of palladium was investigated in the range of Pd $3d_{5/2}$ and $3d_{3/2}$ levels. Binding energies were referred to C1s at 284.8 eV.

3. RESULTS

3.1. Propane Combustion over a Series of Palladium Catalysts

Figure 1 shows the activity of palladium catalysts supported on a series of metal oxides as a function of reaction temperature in the mixture of $S = 2.4$. The catalytic activity of supported palladium strongly depended on the support materials, especially above ca. 600 K. On the Pd/MgO (a), Pd/Al$_2$O$_3$ (c), Pd/SiO$_2$ (d), and Pd/SiO$_2$–ZrO$_2$ (e) catalysts, the propane conversion decreased with the increase in the reaction temperature above ca. 800 K. Similar decrease in
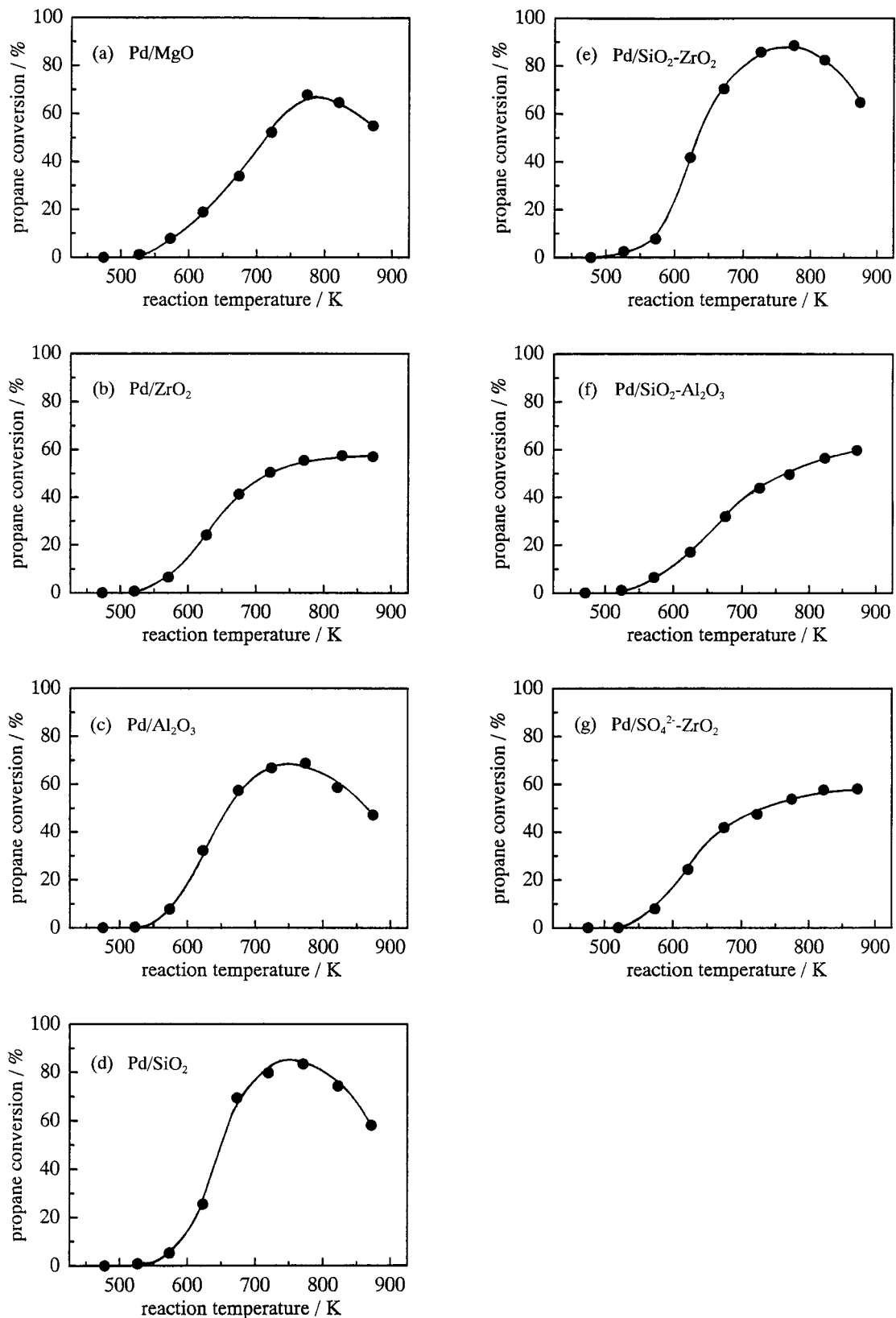
FIG. 1. Propane combustion over a series of palladium catalysts in the mixture of $S = 2.4$.
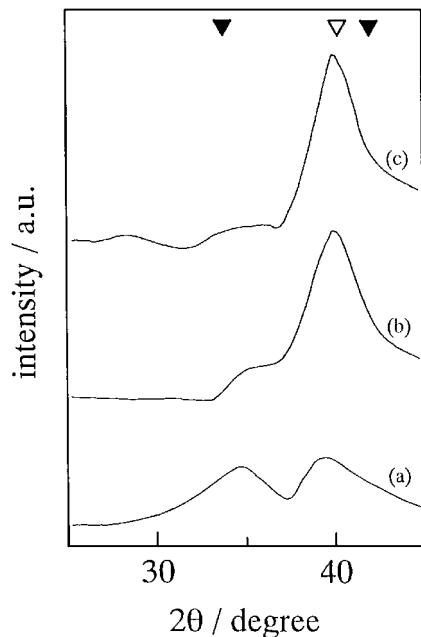
FIG. 2. The subtracted XRD pattern of 5 wt% Pd/Al$_2$O$_3$ after interruption of the catalytic run at 673 K (a), 773 K (b), and 873 K (c) in the mixture of $S = 2.4$. Open symbol, metallic palladium; closed symbols, palladium (II) oxide. The intensities of the profiles were normalized by matching the intensity of the diffraction of Al$_2$O$_3$ at 45.9°, and then the patterns of catalyst were subtracted by that of the support.

the conversion was ascribed to the decomposition of palladium oxide in methane combustion (14–16). In the case of propane combustion, T. Maillet *et al.* confirmed by XRD that the decomposition of palladium oxide is accompanied with the decrease in the conversion (17). In this study, it is also attributed to the decomposition or reduction of palladium oxide, since the diffraction of metallic palladium on the XRD patterns was intensified and that of palladium oxide was weakened with the elevation of the reaction temperature from 673 to 873 K, as shown in Fig. 2. At 773 K, the catalytic activity decreased in the sequence of Pd/SiO$_2$–ZrO$_2$ > Pd/SiO$_2$ > Pd/Al$_2$O$_3$ > Pd/MgO > Pd/ZrO$_2$ > Pd/SiO$_2$–Al$_2$O$_3$ > Pd/SO$_4^{2-}$–ZrO$_2$, while at 673 K, it decreased in the sequence of Pd/SiO$_2$–ZrO$_2$ > Pd/SiO$_2$ > Pd/Al$_2$O$_3$ > Pd/SO$_4^{2-}$–ZrO$_2$ > Pd/ZrO$_2$ > Pd/SiO$_2$–Al$_2$O$_3$ > Pd/MgO. At each temperature, Pd/SiO$_2$–ZrO$_2$ (e) and Pd/SiO$_2$ (d) catalysts were the most active in a series of palladium catalysts under the present condition.

The propane conversion as a function of the acid strength of the support materials is depicted in Fig. 3, which is obtained from the results in Fig. 1. It was clarified that the catalytic activity varies with the acid strength of the support materials; the highest catalytic activity under this condition was obtained on the support whose acid strength was around pKa $= -7$, and palladium supported on more acidic or more basic support was less active. Although the dispersion of palladium also varied with the support materials

as shown in Table 1, the difference in the catalytic activity could not be interpreted by the difference in the dispersion. Therefore, the catalytic activity was suggested to be affected by the acid strength of support materials rather than the dispersion of palladium.

3.2. Propane Combustion in the Various Reaction Mixture

In order to discuss the effect of support materials in further detail, the catalytic activity of some catalysts, Pd/ZrO$_2$, Pd/Al$_2$O$_3$, and Pd/SiO$_2$–Al$_2$O$_3$ was examined under various reaction conditions in the same procedure as in the previous study (6). Figure 4 shows the catalytic activity of the three catalysts at 673 and 773 K under various reaction mixtures ($S = 1.0$–7.2). (The profiles of Pd/SiO$_2$–Al$_2$O$_3$ at each temperature were already reported in the previous study (6)). Over each catalyst, the catalytic activity obviously changed with the S value: with the increase in the S value, the activity reached maximum, and further increase in the S value reduced the activity. The S value giving maximum activity did not change with the reaction temperature, but changed from catalyst to catalyst: it decreased in the sequence of Pd/SiO$_2$–Al$_2$O$_3$ > Pd/Al$_2$O$_3$ > Pd/ZrO$_2$, exhibiting that more acidic support gives maximum activity at higher S value.

3.3. The Dispersion of Palladium

The dispersions of palladium catalysts were measured after interruption of the catalytic run at 773 K. As shown in Tables 2–4, the dispersions after the reaction were not changed with the variation of the S value, and further they were almost the same as that of the prereduced catalyst. These results clearly show that the dispersion of palladium is scarcely affected by the reaction condition.
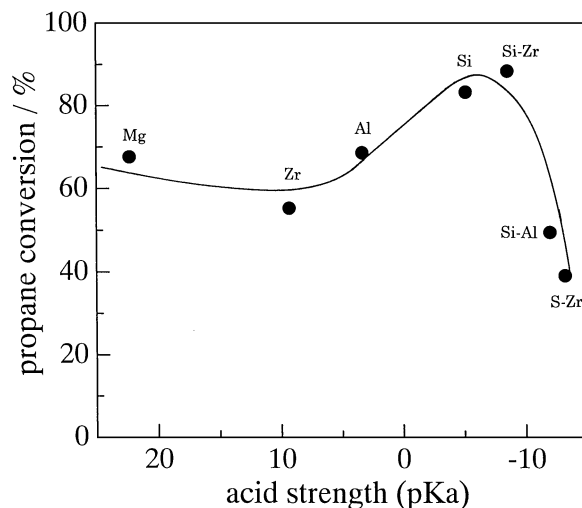

FIG. 3. The activity of palladium catalysts as a function of the acid strength of the support materials in the mixture of $S = 2.4$ at 773 K.
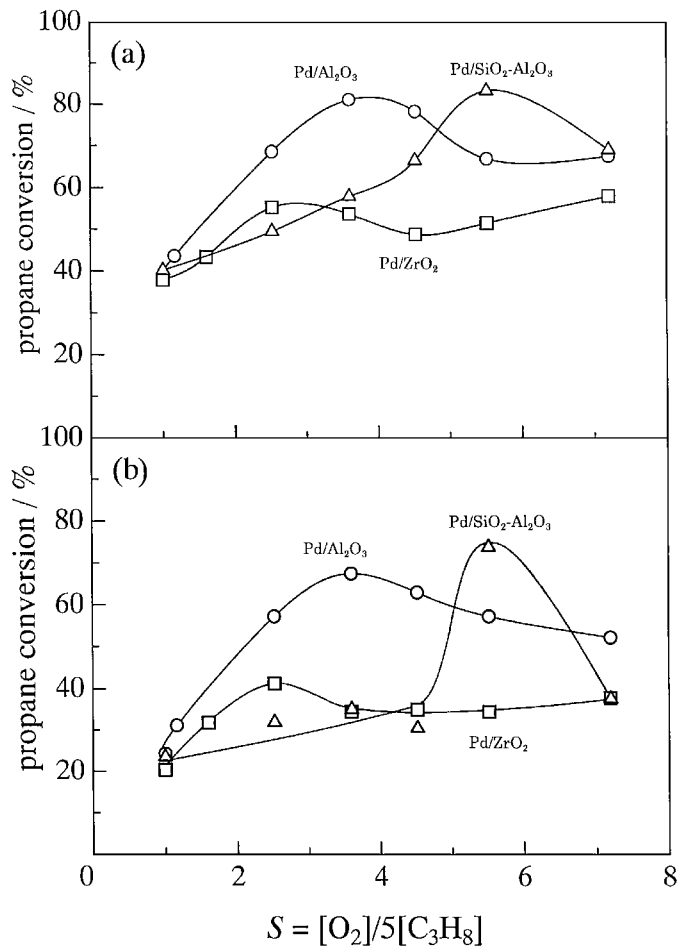
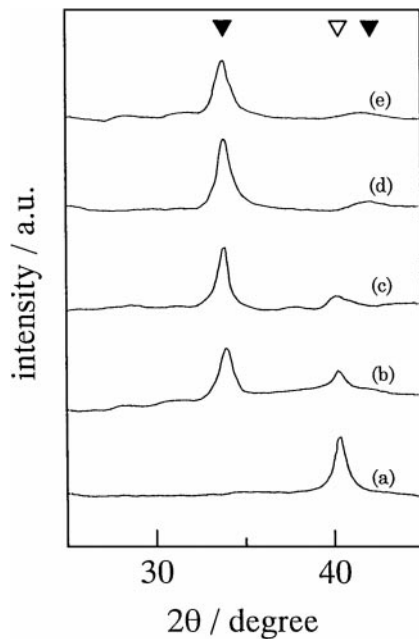FIG. 4. The activity of palladium catalysts as a function of the S value at 773 K (a) and 673 K (b).

FIG. 5. The subtracted XRD pattern of 5 wt% Pd/ZrO$_2$ after prereduction (a), after interruption of the catalytic run at 773 K in the mixture of $S = 1.0$ (b), $S = 2.4$ (c), $S = 5.5$ (d), and after oxidation (e). Open symbol, metallic palladium; closed symbols, palladium (II) oxide. The intensities of the profiles were normalized by matching the intensity of the diffraction of ZrO$_2$ at 28.4°, and then the patterns of catalyst were subtracted by that of the support.

3.4. X-ray Diffraction

The XRD patterns of Pd/ZrO$_2$, Pd/Al$_2$O$_3$, and Pd/SiO$_2$–Al$_2$O$_3$ after interruption of the catalytic run at 773 K are given in Figs. 5–7, respectively. In the case of Pd/ZrO$_2$ (Fig. 5) and Pd/Al$_2$O$_3$ catalysts (Fig. 6), patterns of palladium species were obtained by subtracting the pattern of support from that of catalysts because of too strong diffraction of support. The diffraction line at $2\theta = 40.1°$ (open symbol) is assigned to the metallic palladium and those at $2\theta = 33.9°$ and $42.0°$ (closed symbol) to palladium (II) oxide.

On prereduced Pd/ZrO$_2$ catalysts (Fig. 5a), only the diffraction line of metallic palladium was observed at $2\theta = 40.1°$. After the reaction at $S = 1.0$ and 2.4, i.e., at relatively low oxygen concentration (Figs. 5b and 5c), the diffraction line of metallic palladium and the very broad diffraction

TABLE 2

The Dispersion of Palladium Species and Oxidation State of Palladium on ZrO$_2$ after the Interruption of the Catalytic Run at 773 K

S value [O$_2$]/5[C$_3$H$_8$]	Dispersion (%)	The oxidation state of palladium (XRD)	Fraction of metallic palladium[a] (XPS) (%)	Propane conversion (%)	Reaction rate (μmol/s · g-cat)
After prereduction	16	Pd	65		
1.0	15	Pd, PdO	0	37.9	11.8
2.4	16	Pd, PdO	0	55.4	18.0
5.5	16	PdO	0	51.7	16.6
Oxidation	—[b]	PdO	0		

[a] Calculated from the area intensity of Pd $3d_{5/2}$ core level.
[b] Not measured.

TABLE 3

The Dispersion of Palladium Species and Oxidation State of Palladium on Al$_2$O$_3$ after the Interruption of the Catalytic Run at 773 K

S value [O$_2$]/5[C$_3$H$_8$]	Dispersion (%)	The oxidation state of palladium (XRD)	Fraction of metallic palladium[a] (XPS) (%)	Propane conversion (%)	Reaction rate (μmol/s · g-cat)
After prereduction	25	Pd	85		
1.0	28	Pd	70	38.3	12.6
2.4	24	Pd	10	68.7	22.6
3.6	22	Pd, PdO	0	81.3	28.7
5.5	24	PdO	0	67.1	22.5
7.2	26	PdO	0	67.9	23.3
Oxidation	—[b]	PdO	0		

[a] Calculated from the area intensity of Pd 3$d_{5/2}$ core level.
[b] Not measured.

line of palladium oxide (at $2\theta = 33.9°$) were observed, while only diffraction of palladium oxide was found after the reaction at $S = 5.5$ (Fig. 5d) and after oxidation (Fig. 5e). On Pd/Al$_2$O$_3$ catalysts (Fig. 6), only the diffraction of metallic palladium was observed after prereduction and reaction at $S = 1.0$ and 2.4 (Figs. 6b–6d), while both patterns of metallic palladium and palladium oxide were observed after reaction at $S = 3.6$ (Fig. 6e). There was only the diffraction of palladium oxide after reaction at $S = 5.5$ and 7.2 and after oxidation (Figs. 6f–6h). On Pd/SiO$_2$–Al$_2$O$_3$ catalysts (Fig. 7), only the diffraction of metallic palladium was observed after reduction and reaction at $S = 2.4$ (Figs. 7b and 7c), while there were both patterns of metallic palladium and palladium oxide after reaction at $S = 3.6$ and 5.5 (Figs. 7d and 7e). There was only the diffraction of palladium oxide after reaction at $S = 7.2$ and after oxidation (Figs. 7f and 7g). The oxidation state of palladium after the reaction, thus obtained through XRD patterns, was summarized in Tables 2–4.

On each catalyst, the oxidation of palladium occurs with increase in the S value as shown in Tables 2–4. However, the threshold S value for the oxidation of palladium varied with

the support material and larger threshold S was required on more acidic support: on ZrO$_2$, palladium was oxidized even at $S = 1.0$–2.4, on Al$_2$O$_3$ at $S = 3.6$, and on SiO$_2$–Al$_2$O$_3$ at $S = 3.6$–5.5. This result suggests that the acidic support prevents the oxidation of palladium.

3.5. X-ray Photoelectron Spectroscopy

Figures 8–10 show the XPS spectra of Pd/ZrO$_2$, Pd/Al$_2$O$_3$, and Pd/SiO$_2$–Al$_2$O$_3$ after interruption of the catalytic run at 773 K. The peak of Pd 3$d_{5/2}$ at 335.0–335.1 eV is assigned to metallic palladium, and that at 336.5–336.6 eV to palladium (II) oxide (18–20). The peak of Pd 3$d_{3/2}$ was observed at 5.3 eV higher than that of Pd 3$d_{5/2}$. Very large peaks on Pd/ZrO$_2$ are assigned to Zr 3p.

Similarly to the result of XRD, the oxidation of palladium occurred with the increase in the S value on each catalyst, and palladium on the basic support was more oxidized than that on the acidic support. On Pd/ZrO$_2$ catalysts (Fig. 8), palladium oxide was exclusively observed after the reaction (Figs. 8b–8d). On Pd/Al$_2$O$_3$ catalysts (Fig. 9), both

TABLE 4

The Dispersion of Palladium Species and Oxidation State of Palladium on SiO$_2$–Al$_2$O$_3$ after the Interruption of the Catalytic Run at 773 K

S value [O$_2$]/5[C$_3$H$_8$]	Dispersion (%)	The oxidation state of palladium (XRD)	Fraction of metallic palladium[a] (XPS) (%)	Propane conversion (%)	Reaction rate (μmol/s · g-cat)
After prereduction	6.5	Pd	87		
2.4	6.9	Pd	34	49.6	16.3
3.6	6.3	Pd, PdO	25	58.1	19.2
5.5	7.1	Pd, PdO	12	83.5	26.2
7.2	6.5	PdO	0	69.5	23.1
Oxidation	—[b]	PdO	0		

[a] Calculated from the area intensity of Pd 3$d_{5/2}$ core level.
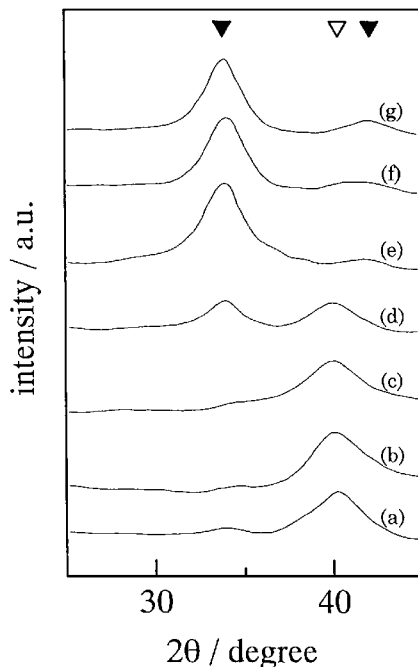[b] Not measured.

FIG. 6. The subtracted XRD pattern of 5 wt% Pd/Al$_2$O$_3$ after prereduction (a), after interruption of the catalytic run at 773 K in the mixture of $S = 1.0$ (b), $S = 2.4$ (c), $S = 3.6$ (d), $S = 5.5$ (e), $S = 7.2$ (f), and after oxidation (g). Open symbol, metallic palladium; closed symbol, palladium (II) oxide. The intensities of the profiles were normalized by matching the intensity of the diffraction of Al$_2$O$_3$ at 45.9°, and then the patterns of catalyst were subtracted by that of the support.

metallic palladium and palladium oxide were seen after the reaction at $S = 1.0$ and 2.4 (Figs. 9b and 9c), while only palladium oxide was observed at higher S value (Figs. 9d–9f). On Pd/SiO$_2$–Al$_2$O$_3$ catalysts (Fig. 10), both metallic palladium and palladium oxide were observed after the reaction at $S \geq 5.5$ (Figs. 10b–10d). The tendency is more clearly shown by the fraction of metallic palladium, shown in Tables 2–4, estimated from curve fitting analysis.

The threshold S value for the oxidation of palladium varied with the support material and larger threshold S was required on more acidic support. The threshold S values obtained from XPS were smaller than that obtained from XRD, showing that the oxidation of palladium occurs from the surface of a palladium particle.

4. DISCUSSION

The catalytic activity was considerably affected by the S value, representing the oxygen concentration relative to the stoichiometric one, and passed through the maximum with the increase in S value, as shown in Fig. 4. As shown in Tables 2–4, the oxidation state of palladium estimated by XRD and XPS also changed with the S value; palladium was more oxidized under the condition of higher S value. In

contrast, the dispersion of palladium was scarcely affected by the S value.

The correlations between the S value and the catalytic activity, and between the S value and the oxidation state differed form catalyst to catalyst. However, the correlation between the oxidation state and catalytic activity was common to all catalysts. In the case of Pd/Al$_2$O$_3$, the increase in the S value brought about enhancement of the catalytic activity and the partial oxidation of palladium in the range of $1.0 \leqq S \leqq 3.6$. However, further increase in the S value brought about a decrease in the activity and the complete oxidation of palladium. Thus, partially oxidized palladium was found to show the highest catalytic activity. In a similar manner, palladium on ZrO$_2$ or SiO$_2$–Al$_2$O$_3$ showed the highest activity when palladium was partially oxidized. In the previous paper, the authors concluded that the variation in the activity in various mixtures is arisen from the variation in the oxidation state of palladium and partially oxidized palladium is most active for propane combustion over Pd/SiO$_2$–Al$_2$O$_3$ (6). The conclusion seems not to be characteristic of Pd/SiO$_2$–Al$_2$O$_3$ but to be applied for other palladium catalyst, probably as a general rule.

It is obvious from the above discussion that the change in catalytic activity with support materials may be attributed to, at least as one of the factors, the change in the
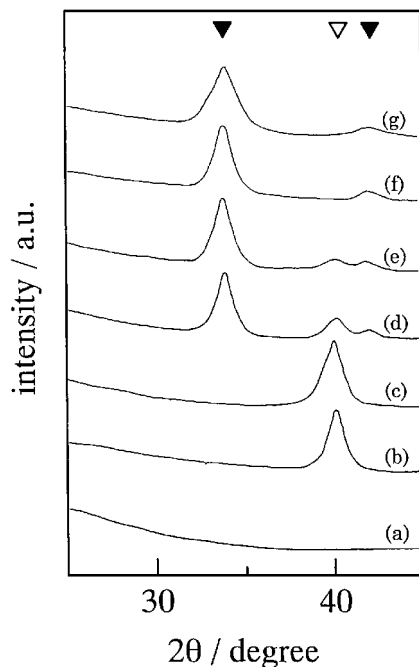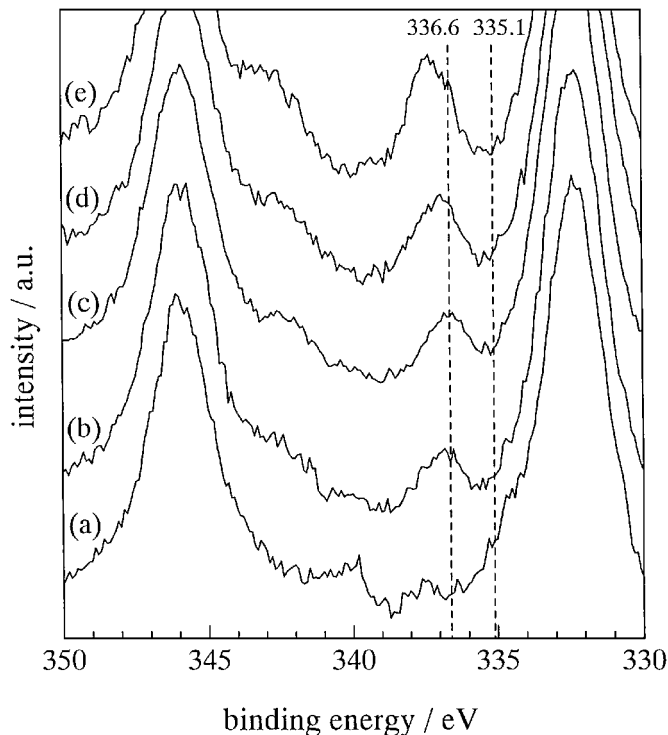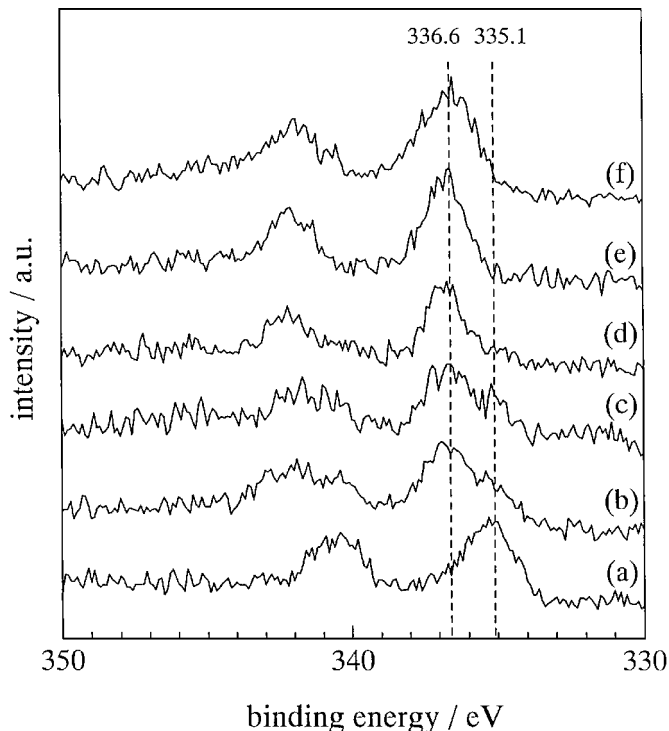

FIG. 7. The XRD pattern of SiO$_2$–Al$_2$O$_3$ (a) and 5 wt% Pd/SiO$_2$–Al$_2$O$_3$ after prereduction (b), after interruption of the catalytic run at 773 K in the mixture of $S = 2.4$ (c), $S = 3.6$ (d), $S = 5.5$ (e), $S = 7.2$ (f), and after oxidation (g). Open symbol, metallic palladium; closed symbols, palladium (II) oxide. The intensities of the profiles were normalized by matching the intensity of the diffraction of SiO$_2$–Al$_2$O$_3$ around 24°. These XRD patterns have already reported in Ref. (6).

FIG. 8. XPS Pd 3d spectra of Pd/ZrO₂ after reduction (a), after the interruption of the catalytic run at 773 K in the mixture of $S = 1.0$ (b), $S = 2.4$ (c), $S = 5.5$ (d), and after oxidation (e).

FIG. 10. XPS Pd 3d spectra of Pd/SiO₂–Al₂O₃ after reduction (a), after the interruption of the catalytic run at 773 K in the mixture of $S = 2.4$ (b), $S = 3.6$ (c), $S = 5.5$ (d), $S = 7.2$ (e), and after oxidation (f). These spectra have already reported in Ref. (6).
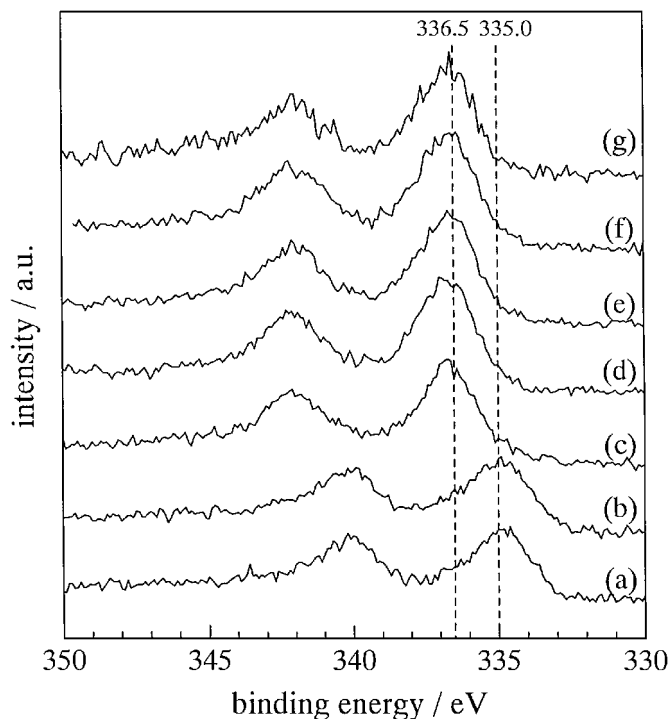
FIG. 9. XPS Pd 3d spectra of Pd/Al₂O₃ after reduction (a), after the interruption of the catalytic run at 773 K in the mixture of $S = 1.0$ (b), $S = 2.4$ (c), $S = 3.6$ (d), $S = 5.5$ (e), $S = 7.2$ (f), and after oxidation (g).

oxidation state of palladium. In other words, the support material affects the catalytic activity through the control of resistibility of supported palladium against the oxidation. The order of resistibility against oxidation corresponds to Pd/SiO₂–Al₂O₃ > Pd/Al₂O₃ > Pd/ZrO₂. Although it was reported that small palladium particle was oxidized easier than large one (21), this order dose not correspond to that of dispersion after the reaction, Pd/SiO₂–Al₂O₃ > Pd/ZrO₂ > Pd/Al₂O₃. This suggests that the resistibility is affected by the support materials more than by the dispersion. The order of resistibility is in good agreement with the order of the acid strength of support materials: SiO₂–Al₂O₃ > Al₂O₃ > ZrO₂. The agreement between the sequences may indicate that the palladium on acidic support has resistibility against the oxidation, or, in other words, the acidic support prevents the oxidation of supported palladium.

The change in the activity of a series of palladium catalysts, shown in Fig. 3, may be explained by difference in the oxidation state, which would be controlled by the acid strength of support materials. In this reaction condition ($S = 2.4$), the catalytic activity was the highest on SiO₂ and SiO₂–ZrO₂. At $S = 2.4$, as shown in Tables 2–4, palladium was in the metallic state on SiO₂–Al₂O₃ (more acidic than SiO₂ and SiO₂–ZrO₂), partially oxidized on Al₂O₃ (more basic), and fully oxidized on ZrO₂ (much more basic). Thus,

palladium on SiO_2 and SiO_2–ZrO_2 is considered to have an intermediate oxidation state between those on SiO_2–Al_2O_3 and Al_2O_3, which seems to correspond well to the highest activity among the catalyst examined.

From above discussion, some conclusions can be deduced as follows: (I) Partially oxidized palladium is most active for propane combustion. (II) Acidic supports prevent the oxidation of palladium, and, on the contrary, basic supports accelerate the oxidation of palladium. These conclusions can be applied for the design of the active palladium catalyst; that is, the more acidic support is proper for the more oxidizing mixture and vice versa.

The support effect, prevention of oxidation of metal by the acidic support, would be expected in other metal catalysts. For example, in propane combustion over platinum catalyst, Ishikawa *et al.* reported that platinum on acidic support shows higher activity than that on basic support (10). Taking into consideration that metallic platinum is most active in methane combustion over platinum catalyst (22), their result is anticipated to indicate that acidic support prevent platinum from the oxidation, to maintain high catalytic activity.

Additional effect of strongly basic support may be seen from Figs. 3 and 4. As shown in Fig. 4, Pd/ZrO_2 showed relatively low activity in comparison with Pd/Al_2O_3 and Pd/SiO_2–Al_2O_3, and the activity of Pd/ZrO_2 increased with further increase in S value above 4.5. In Fig. 3, further, Pd/MgO was more active than Pd/ZrO_2. Under these conditions, e.g., under the higher oxidizing conditions or on more basic support, a new palladium species, such as a conjugated oxide with support or more oxidized species as $MgPd_3O_4$ or Mg_2PdO_4 (23), might be formed to exhibit higher catalytic activity. Further study is in progress on the catalytic combustion under highly oxidizing conditions.

5. CONCLUSIONS

The conclusions in the present paper are the following: (I) Although both of the dispersion and the oxidation states of palladium affect the catalytic activity of palladium supported on a series of supports, the oxidation state of palladium affects the catalytic activity more than the dispersion; the partially oxidized palladium shows the highest catalytic activity for propane combustion. (II) The oxidation state of supported palladium is affected by the acid strength of the support material; the acidic support materials prevent the oxidation of supported palladium.

These conclusions would lead to a proposal that the acid strength of support materials is an effective parameter for the design of active palladium catalyst: the acidic support should be selected for highly oxidizing reaction condition and vice versa.

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