Catalytic Properties of Pd-Supported Hexaaluminate Catalysts for High-Temperature Catalytic Combustion

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The catalytic properties of palladium supported on hexaaluminates ($Sr_{0.8}La_{0.2}XAl_{11}O_{19}$, X = Al and Mn) was studied for use in high-temperature catalytic combustion. The activity of Pd/$Sr_{0.8}La_{0.2}Al_{12}O_{19}$ increased initially with a rise in temperature, but decreased at high temperatures (ca. 700°C). The drop in catalytic activity became pronounced when the supported Pd particles were sintered into large agglomerates after calcination above 1000°C. From *in situ* XRD, TPD, and TPRO, it was revealed that the activity drop accompanies dissociated of PdO into metallic Pd species. Since the dissociation of PdO is a thermodynamic function of oxygen partial pressure, the temperature at the conversion drop appeared was influenced by the oxygen concentration in the combustion reaction. The dissociation of PdO appears to result in removal of adsorbed oxygen species necessary for the catalytic reaction. On the other hand, such a significant drop in catalytic activity can be avoided by the use of Mn-substituted hexaaluminate (X = Mn) as a catalyst support. The catalytic activity of Mn-substituted hexaaluminate is effective in compensating for the drop in activity of Pd so that a stable combustion reaction can be attained in a whole temperature range.
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INTRODUCTION

The use of oxidation catalysts in a combustor has been an important subject in suppressing emissions of nitrogen oxides. A peak temperature above 1500°C in a conventional flame combustion can be reduced to ca. 1300°C by means of catalytically stabilized fuel-lean combustion, in which thermal NO_x formation is negligible. For the practical application of catalytic combustors, the development of thermally stable catalyst materials is one of the important issues because high operation temperature (>1200°C) immediately deteriorates any conventional oxidation catalysts. Another difficulty for the combustion application lies in the wide range of reaction temperatures, i.e., the catalyst needs to cover several different kinetic processes and/or their transient regions. At the inlet part of a catalyst zone combustion is initiated as kinetically controlled surface reaction, since the catalyst temperature is low after the initiation, the exothermic surface reaction enhances the temperature along the axial direction. Then the overall reaction is determined by a mass transfer process. A further increase of temperature initiates gas-phase reaction so that catalyst temperature reaches the maximum (>1200°C) (*1*).

We have previously reported that a new catalyst material based on hexaaluminate compounds show excellent thermal stability in maintaining a large surface area above 1300°C (*2, 3*). Since partial substitution Mn for Al significantly promotes catalytic reaction due to high reduction–oxidation activity of Mn species, Mn-substituted hexaaluminate demonstrates high thermal stability and catalytic activity necessary for a back end zone of the combustor catalyst (*4–6*). On the other hand, the catalyst for the inlet part should possess higher catalytic activity to initiate the surface reaction at low temperatures. One of the promising active

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species is palladium, which is known to show not only the highest activity for the catalytic oxidation of methane but also the lowest volatility among noble metal catalysts. In fact, most research done to date concentrates on supported Pd catalysts (7–12). However, these previous studies were limited to the catalytic behavior at low temperature. Information on the high-temperature reactions is strongly required from the viewpoint of the catalytic behavior.

In the present study, we have studied the catalytic activity of Pd catalysts supported on hexaaluminates for use in the high-temperature catalytic combustion of methane. Temperature dependence of catalytic activity was discussed with reference to the phase equilibrium of Pd species, which plays a key role especially in the high reaction temperatures.

EXPERIMENTAL

Sample Preparation and Characterization

Neat and Mn-substituted hexaaluminate supports ($Sr_{0.8}La_{0.2}XAl_{11}O_{19}$, X = Al and Mn, which are referred to as SLA and SLMA, respectively) were prepared from hydrolysis of metal alkoxides. Calculated amounts of Sr metal and $Al(OC_3H_7)_3$ were vigorously stirred in 2-propanol at 80°C for 3 h. After dissolution was complete, an aqueous solution of $La(NO_3)_3$ and/or $Mn(NO_3)_2$ was added to the alcoholic solution. The resultant gel was dried and calcined at 1200°C for 5 h in air. Palladium was deposited on the hexaaluminate supports by impregnation of palladium(II) nitrate followed by calcination at 1000–1400°C for 5 h in air. The loading amount of palladium metal was 1.44 wt%.

Specific surface area of catalysts was determined by the BET method using nitrogen adsorption. Transmission electron microscopy (TEM) was used to observe the palladium on the hexaaluminate supports. To obtain particle size distributions of palladium, 100 Pd particles were observed.

Catalytic Combustion of Methane

Catalytic combustion of methane over supported palladium catalysts were exam-ined in a conventional flow reactor at atmospheric pressure. Catalysts were fixed in a quartz tube by packing alumina beads at both ends of the catalyst bed. A gaseous mixture of CH_4 (1 vol%), O_2 (2.2–25 vol%), and N_2 (balance) was supplied at a space velocity of 48,000 h^{-1}. Methane conversion in the effluent gas was analyzed by online gas chromatography.

Methane combustion was also carried out in a pulse reactor. Prior to the reaction, a sample (0.2 g) was preheated in oxygen and in helium stream (50 ml/min) at 800°C for 2 h in order to convert palladium species into oxide (PdO) and metallic (Pd) states, respectively. After cooling in the same atmosphere to 370°C and keeping for 1 h, 1 cm^3 of a gaseous mixture of CH_4 (6 vol%), O_2 (14 vol%), and N_2 (balance) was pulsed to the catalyst in a helium stream. Methane conversion is effluent gas was analyzed by TCD.

In Situ X-Ray Diffraction over Pd/Hexaaluminates

In situ X-ray diffraction was used for observing the of crystalline phases of palladium species on the hexaaluminate supports in a gas mixture (CH_4, vol% and air, 99 vol%). Heating and cooling to the desired temperatures at a constant rate (10°C/min). The XRD profile was recorded after holding for 30 min at each temperature. This single step was repeated every 50° from 400 to 950°C.

Temperature-Programmed Desorption of Oxygen and Temperature-Programmed Reoxidation

Temperature-programmed desorption of oxygen (TPD) was measured in a flow system. Prior to the measurement the sample was heated in an oxygen stream (50 ml/min) at 800°C for 2 h followed by cooling in a same atmosphere to room temperature. After evacuation, the sample was heated up to 1000°C at a constant rate (10°C/min) in a helium stream (50 ml/min). After the TPD measurement and subsequent evacuation at

TABLE 1

BET Surface Area (m^2 g^{-1}) of 1.44 wt% Pd/Sr$_{0.8}$La$_{0.2}$XAl$_{11}$O$_{19}$ (X = Al, Mn)

	Calcination temperature (°C)		
	1000	1200	1400
X = Al	25.3	19.7	12.2
X = Mn	26.6	16.9	12.1

room temperature the sample was heated again at the same rate in the stream of gas mixture (O$_2$, 5 vol%, He balance, 50 ml/ min) to record a temperature programmed reoxidation (TPRO). The oxygen in the effluent gas was detected by using a TCD cell.

RESULTS

Surface Area and Microstructure of Catalysts

Retention of large surface area and/or porous microstructure at combustion temperatures is essential for combustion catalysts. Because of the excellent thermal stability of hexaaluminate supports, the BET surface areas of Pd/SLA and Pd/SLMA catalysts listed in Table 1 show no serious decrease even after calcination at 1400°C. Microstructure and particle size of as prepared catalysts were observed by TEM. Figure 1 shows the typical micrograph of the Pd catalyst supported on hexaaluminate after calcination at 1200°C. As reported previously (13), hexaaluminates crystallizes as hexagonal platelets of which the basal plane is normal to the c axis. Such a crystal morphology derived by anisotropic crystal growth seems effective in retaining high specific surface area even above 1200°C. Palladium can be observed as highly dispersed fine particles (ca. 17 mm in diameter) deposited on the basal plane of hexaaluminate. The particle size of hexaaluminate facet was almost independent of calcination temperature. However, the calcination at elevated temperatures caused the significant growth of palladium particles.

Catalytic Combustion of Methane over Pd/Hexaaluminate

Catalytic combustion of methane was performed over Pd/SLMA and Pd/SLA catalysts with various calcination temperatures (1000–1400°C). Figure 2 shows the temperature dependence of methane conversion over Pd/SLA catalysts. When the SLA support with low catalytic activity was submitted to the reaction, combustion appears to be initiated by the radical formation at the surface of the support material and to progress through a chain reaction in the gas phase. This can be characterized by the high initiation temperature and the steep rise in methane conversion. By supporting Pd as the active species, the initiation temperature could be significantly reduced to 300°C regardless of the calcination temperature of the catalyst. Over the supported Pd catalysts, however, complete combustion required higher temperature than that for unsupported catalyst (SLA). This is partly because the overall reaction over Pd species levels off due to a mass transfer limitation at a high converison level. In addition, the mass transfer limitation means that the surface fuel concentration is nearly zero. For the initiation of gas-phase reaction, a certain concentration of methane needs to bring about radical formation (i.e., CH$_3$·) near the surface. Besides these complicated reaction mechanisms, the following unique catalytic behavior of the Pd catalyst also inhibited to complete the reaction, being a serious problem in using supported Pd catalyst for catalytic combustion reaction.

As can be seen in Fig. 2, catalytic activity of the supported Pd catalysts is strongly dependent on the calcination temperature. After initiation of the reaction, the conversion increased up to ca. 700°C, but decreased with a rise in reaction temperature between ca. 700 and ca. 850°C. As a result of this negative temperature coefficient region, the temperature dependence of the catalytic activities showed the minimum at ca. 800°C. It should be noted that this drop in activity
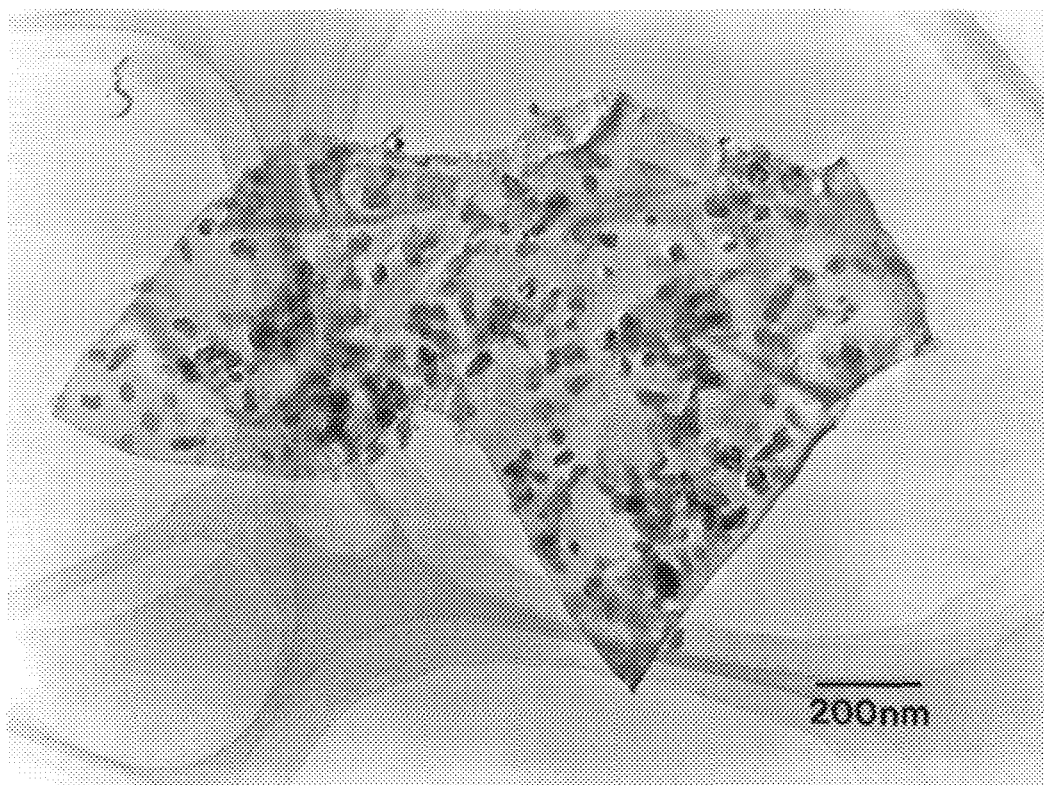
FIG. 1. TEM photograph of 1.44 wt% $Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}$ calcined at 1200°C.
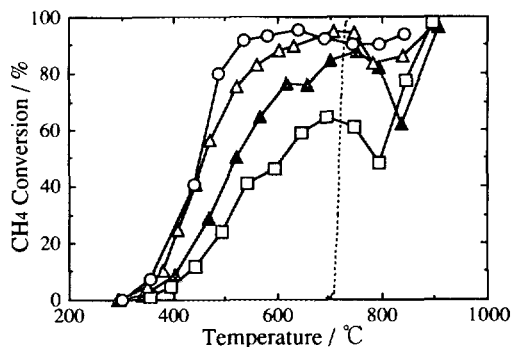

FIG. 2. Catalytic combustion of methane over 1.44 wt% $Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}$. Calcination temperature: (O) 1000, (△) 1200, (▲) 1300, and (□) 1400°C. The reaction over $Sr_{0.8}La_{0.2}Al_{12}O_{19}$ calcined at 1200°C is also shown as the broken line. Reaction conditions: CH_4, 1 vol%; O_2, 20 vol%; N_2, balance; space velocity, 48,000 h^{-1}.

was more drastically observed when the supported Pd catalyst was calcined at elevated temperatures. This effect of the calcination temperature indicates that methane combustion should be highly sensitive to the particle size of palladium species.

The Mn-substituted hexaaluminate, SLMA, in which Mn ions occupied Al sites in the hexaaluminate structure play a role as reduction-oxidation species, showed relatively high catalytic activity for methane combustion (Fig. 3). By supporting Pd on SLMA, the slightly increased catalytic activity was observed for the sample after calcination below 1200°C. However, the most promising effect is the absence of the significant drop of methane conversion, and thus complete combustion could be achieved at low temperatures as compared with the Pd/SLA catalysts.
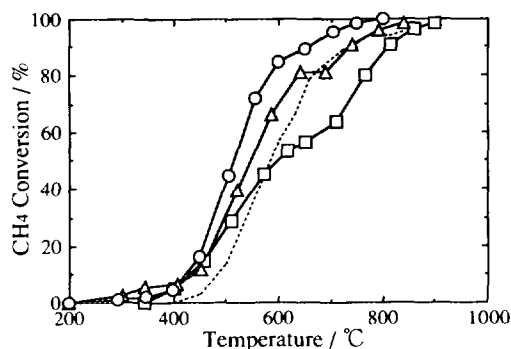
FIG. 3. Catalytic combustion of methane over 1.44 wt% $Pd/Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$. Calcination temperature: (○) 1000, (△) 1200, and (□) 1400°C. The reaction over $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ calcined at 1200°C is also shown as the broken line. Reaction conditions: CH_4, 1 vol%; O_2, 20 vol%; N_2, balance; space velocity, 48,000 h^{-1}.

In Situ X-Ray Analysis of Pd Species

It was revealed that the Pd catalyst supported on SLA showed complicated catalytic behavior at the high temperature region. This was observed for Pd catalysts supported on other materials, such as alumina (14), which are closely related to the chemical state of Pd species. Thus, in situ X-ray diffraction was employed to qualitatively analyze the Pd species present under catalytic reaction conditions. Figure 4 shows a typical X-ray diffraction pattern of Pd/SLA. Of the diffraction lines from PdO and Pd only the strongest diffraction line due to metallic Pd which is located at $2\theta = 40.1°$, could be clearly observed because of overlapping with the lines of hexaaluminate.
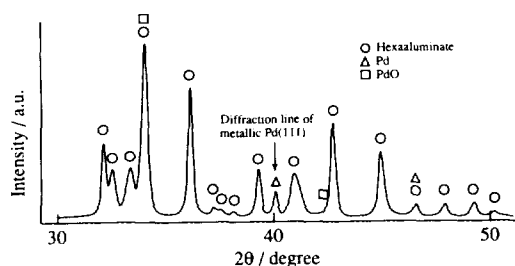

FIG. 4. X-ray diffraction pattern of 1.44 wt% $Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}$ calcined at 1200°C.
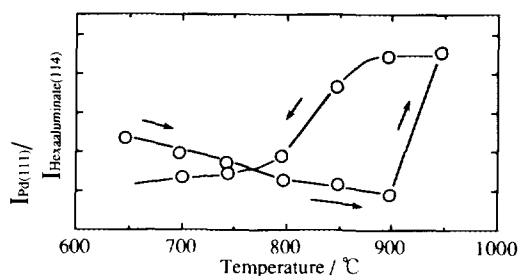

FIG. 5. Change in relative peak intensity of Pd with heating and cooling treatment in a stream of gas mixture of CH_4 (1 vol%) and air (99 vol%). Sample was calcined at 1200°C in advance.

The intensity of the Pd(111) line was changed with temperature, while no appreciable change was observed for the diffraction pattern of hexaaluminate. Figure 5 shows the change of the relative peak intensity between Pd(111) and hexaaluminate(114) when the Pd/SLA sample was heated in a stream of gas mixture of CH_4 (1 vol%) and air (99 vol%). An XRD pattern measured at room temperature indicated the presence of metallic Pd and PdO. The intensity of this line, which gradually decreased with a rise in temperature up to 900°C, showed a precipitous increase from 900°C. On the contrary, when the sample was cooled to ca. 700°C, the intensity of diffraction line was weakened again to the original intensity. From a simple comparison with the temperature dependence of catalytic activity as shown in Fig. 2, the phase transformation must be closely related to the complicated catalytic property of supported Pd catalysts at high temperature.

Analysis of Redox Property by TPD and TPRO

To elucidate the relation between catalytic property and phase transformation of the supported Pd catalyst, the reduction-oxidation property was studied by TPD of oxygen and TPRO. Figure 6 shows TPD and TPRO profiles of Pd/SLA calcined at 1000, 1200, and 1400°C. Although no desorption was observed for the SLA support, the sup-
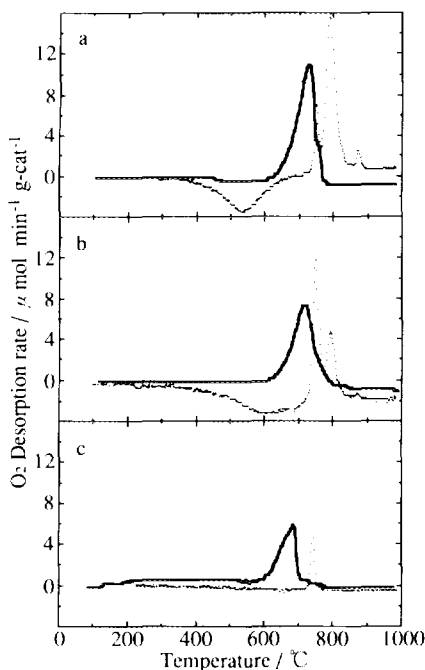
FIG. 6. TPD (solid line) and TPRO (dotted line) profiles of 1.44 wt% $Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}$ (Pd/SLA) calcined at (a) 1000, (b) 1200, and (c) 1400°C.

ported Pd catalyst equally showed the single desorption peak at ca. 700°C, which can be ascribed to the dissociation of PdO into Pd from the *in situ* XRD measurement (Fig. 5). For the Pd/SLA calcined at 1000°C, the total amount of oxygen desorption corresponds to the conversion of all the Pd species into PdO. However, the amount of oxygen desorption decreased with an increase in calcination temperature. This is probably because of partial inclusion of metallic Pd and an increase of particle size at higher calcination temperatures.

After TPD measurement, the sample was heated in the presence of oxygen to record its TPRO profiles. For every sample, reoxidation took place above 400°C, but the oxygen incorporated into the catalyst was emitted above 700°C as well as in the TPD measurement. Since the O_2 uptake below 700°C is nearly equal to O_2 desorption above 700°C, a reversible reoxidation of Pd species proceeds in the TPRO process. In this case,

however, the effect of calcination temperature can be seen not only in the amount of oxygen uptake/desorption but also in the number of the desorption peaks. While the sample calcined at 1000°C showed three desorption peaks above 700°C, only a single peak can be observed after calcination at 1400°C.

Figure 7 compares TPD/TPRO profiles of Pd/SLA, Pd/SLMA, and SLMA. The partial substitution of Mn for Al in the hexaaluminate lattice generates the reversible oxygen desorption due to the reduction/oxidation in the lattice. Therefore, the desorption and uptake of oxygen appeared in the TPD and TPRO profiles of Pd/SLMA is the combination the redox reaction of Pd species and SLMA.

Catalytic Properties under Various Oxygen Partial Pressures

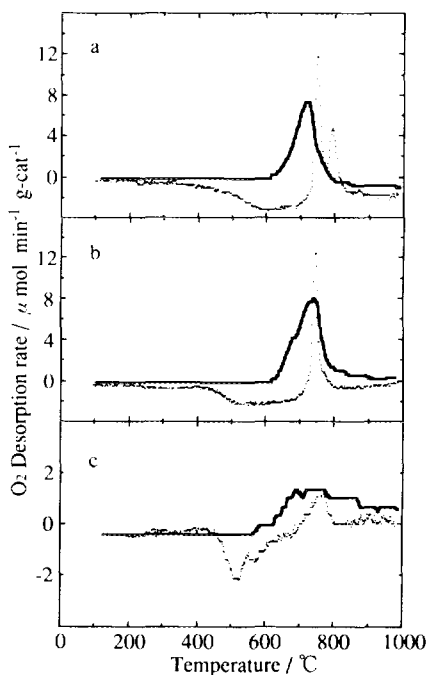*In situ* XRD, TPD, and TPRO results suggest that supported Pd catayst is partly com-

FIG. 7. TPD (solid line) and TPRO (dotted line) profiles of (a) 1.44 wt% $Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}$ (Pd/SLA), (b) 1.44 wt% $Pd/Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (Pd/SLMA), and (c) $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (SLMA). Each sample calcined at 1200°C.
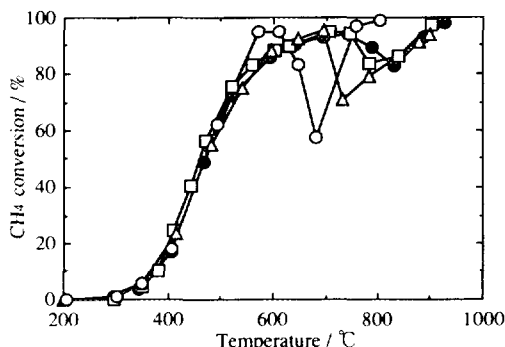
FIG. 8. Temperature dependence of catalytic combustion of methane over 1.44 wt% Pd/Sr$_{0.8}$La$_{0.2}$Al$_{12}$O$_{19}$. Each sample was calcined at 1200°C. Oxygen partial pressure: (○) 2.2, (△) 10, (□) 20, and (●) 23 vol%. Reaction conditions: CH$_4$, 1 vol%; N$_2$, balance; space velocity, 48,000 h^{-1}.

posed of PdO at low temperatures, which decomposes during the catalytic reaction to produce metallic Pd species. The dissociation of PdO accompanied the significant decrease in catalytic activity in Fig. 2. To demonstrate this relation between the dissociation of PdO and the catalytic activity, the effect of oxygen partial pressure on the methane conversion should be examined. Figure 8 shows the results of methane combustion over Pd/SLA under various oxygen partial pressures. The methane conversion below 50% was independent of oxygen concentration, suggesting zero-order kinetics with respect to oxygen partial pressure at higher temperatures, the valley was commonly observed in every conversion curve. The temperature at the minimum conversion between 600 and 1000°C was reduced with a decrease in oxygen concentration. This is consistent with the ease of PdO dissociation at low partial pressures. The drop in methane conversion tended to be significant at low oxygen partial pressures.

The effect of oxygen concentration on the catalytic activity was also examined for the Pd/SLMA catalyst (Fig. 9). In this case, however, the methane conversion curve scarcely depended on inlet oxygen concentration above 10 vol%. The conversion drop

in high conversion region appeared only at 2.2 vol% of inlet oxygen concentration. Consequently, it can be deduced that the decrease in catalytic activity accompanied by dissociation of PdO can be avoided by using SLMA as a support material.

DISCUSSION

Catalytic Activity and Dissociation of PdO

This study reveals the relation between the catalytic activity and the dissociation of PdO. As shown in Figs. 8 and 9, temperature at the valley in the conversion curve depends on the oxygen partial pressure. Theoretical dissociation temperature of PdO can be calculated from the temperature dependence of formation energy as shown in the following equation (15):

$$dG = -27013 + 14.0 \, T \log T - 6.16 \\ \times 10^{-3} \, T^2 - 0.1 \times 10^5 \, T^{-1} \\ - 12.190 \, T \pm 100 \quad (\text{cal/mol}).$$

The result is shown in Fig. 10 as a function of oxygen partial pressure. This figure also shows the P_{O_2} dependence of the temperature at which the slope of conversion curve in Figs. 8 and 9 turned to negative. Since these temperatures agree with the theoretical dissociation temperature of PdO, the
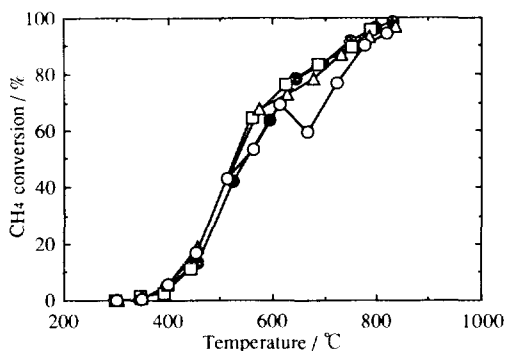

FIG. 9. Temperature dependence of catalytic combustion of methane over 1.44 wt% Pd/Sr$_{0.8}$La$_{0.2}$Al$_{12}$O$_{19}$. Each sample was calcined at 1200°C. Oxygen partial pressure: (○) 2.2, (△) 10, (□) 20, and (●) 23 vol%. Reaction conditions: CH$_4$, 1 vol%; N$_2$, balance; space velocity, 48,000 h^{-1}.
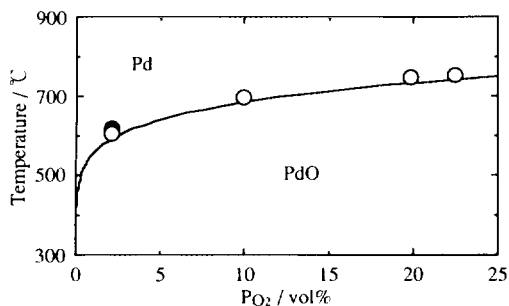
FIG. 10. P_{O_2} dependence of the temperature at which the slope of conversion curve in Figs. 8 and 9 turned to negative. The solid line indicates equilibrium temperature of dissociation of PdO: (O) 1.44 wt% Pd/$Sr_{0.8}La_{0.2}Al_{12}O_{19}$ and (●) 1.44 wt% Pd/$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$.

negative slope in conversion curves should be generated by the dissociation of PdO. Thus, the drop in catalytic activity is brought about by decomposition of PdO into Pd on the support.

The difference of catalytic activity between PdO and Pd was examined by pulse reaction over the Pd/SLA catalyst. After oxidation or reduction treatment to form PdO or Pd, respectively, methane oxidation was performed as pulse reactions in a He stream at the same temperature (370°C) as described in the Experimental section. As was evident from Fig. 11, PdO retained much higher activity than metallic Pd. These results are consistent with the literature of Farrauto *et al.* (*14*) who reported the decrease in conversion of methane in the catalytic combustion over supported Pd catalysts. They also attributed this phenomenon to decomposition of PdO from comparison of methane oxidation with TGA profiles of Pd/Al_2O_3 catalysts. High-temperature oxidation of supported Pd catalysts has been developed by many researchers. Chen and Ruckenstein (*16*) proposed from their TEM study that oxidation breaks up the palladium particles into smaller pieces. Hicks *et al.* (*10*) have reported that palladium oxide exposes new surfaces after oxidation treatment which participate in catalytic oxida-

tion. In other words, surface oxygen species are believed to play a key role in catalytic oxidation of methane over Pd/SLA. Mezaki and Watson (*17*) reported that oxygen adsorption easily proceeded as compared with the subsequent reaction between adsorbed oxygen and CH_4 from their kinetic study of methane oxidation over Pd/Al_2O_3. This is supported by present study which shows that the reaction rate is zero order with respect to oxygen partial pressure at relatively low temperatures (Fig. 8).

One interesting matters speculated from this result is the reaction mechanisms over PdO and Pd. At low temperatures, the catalyst surface is composed of PdO, which is abundant in active surface oxygen site. An increase in reaction temperature brings about the steep rise in methane conversion. When the reaction temperature reaches the dissociation temperature of PdO, however, drastic removal of surface and bulk oxygen leads to lack of active surface oxygen species, resulting in the significant drop in methane conversion. The extent of the activity drop became signficant with increasing calcination temperature of the catalyst (Fig. 2). From TPD/TPRO measurement, sintering of Pd species causes a loss in their surface area and thus depletion of reversibly adsorbed oxygen species. Resultant lack of oxygen species may lead to more serious deactivation at the dissociation temperature
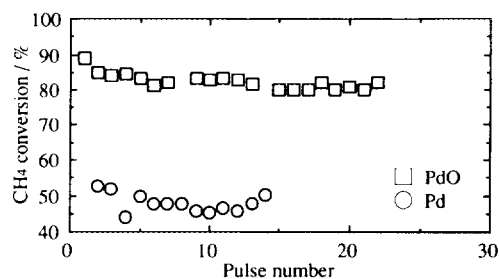

FIG. 11. Activity of 1.44 wt% Pd/$Sr_{0.8}La_{0.2}Al_{12}O_{19}$ calcined at 1200°C with (□) oxidized and (O) reduced Pd at 370°C. Reaction conditions: catalysts, 0.2 g; gas flow rate, 5.52 cm^3/min; pulse gas, 1 cm^3 (CH_4, 6 vol%; O_2, 14 vol%; N_2 balance).

of PdO. Above this temperature, a whole oxidation reaction rate is under limitation of oxygen adsorption onto Pd species. Since the methane conversion increases again with an increase in reaction temperature because of thermal activation of the metallic Pd surface.

Catalytic Activity of Pd/Mn-Substituted Hexaaluminate

The activity drop at the dissociation temperature of PdO could be observed only at very low oxygen partial pressures by using SLMA as a support material (Fig. 3). The TPD/TPRO profiles of Pd/SLMA consist of a simple combination of those from Pd and SLMA, showing no interaction between Pd species and Mn-substituted hexaaluminate. The only difference from Pd/SLA is due to the catalytic activity of SLMA, which is provided by reversible oxygen species accompanied by the reduction-oxidation cycle of Mn in the hexaaluminate lattice. Although the apparent catalytic activity of SLMA is much lower than that of Pd species at low temperatures, their activities became comparable at around the dissociation temperature of PdO. This leads to parallel catalytic reactions for Pd species and SLMA. In such a situation, the activity drop due to dissociation of PdO can be compensated by the catalytic reaction over SLMA support.

The use of catalytically active support materials as SLMA is one possible way to overcome the unstable catalytic activity of the supported palladium catalyst.

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