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# Oxidation of methane over Pd/mixed oxides for catalytic combustion

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## Abstract

Palladium catalysts supported on mixed oxides (Pd/$Al_2O_3$–$MO_x$; M=Co, Cr, Cu, Fe, Mn, and Ni) were investigated for the low-temperature catalytic combustion of methane. Although the surface area decreased with increasing NiO in Pd/$m$$Al_2O_3$–$n$NiO, Pd/$Al_2O_3$–36NiO demonstrated an excellent activity due to the small particle size of palladium. Also, the catalytic activity strongly depended on the composition of the support. Temperature-programmed desorption of oxygen revealed that the catalytic activity in the low-temperature region depends on the adsorption state of oxygen on palladium. The activity was enhanced when the amount of adsorbed oxygen increased. In-situ XRD analysis indicated that the PdO phase was thermally stabilized on Pd/$Al_2O_3$–36NiO. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Catalytic combustion; Catalytic ignition; Temperature-programmed oxygen desorption; Mixed oxides supports based on alumina; Supported PdO catalysts

## 1. Introduction

High-temperature catalytic combustion has been proposed and extensively studied from the viewpoint of achieving low $NO_x$ emission as well as high combustion efficiency for some applications, such as in gas turbines [1]. For an increase in efficiency and decrease in $NO_x$ emissions, it is required to keep the actual combustion temperature rather low as compared with that of flame combustion. Depending on the design of the catalytic combustion system, catalysts are exposed to a wide temperature range, that is 500–1300°C. Therefore, two different specifications are sometimes required for the catalysts: (1) high catalytic activity for a low ignition temperature; and (2) high heat resistance to catalytic activity, surface area and thermal shock. High thermal stability becomes a more important property rather than the catalytic activity in the down stream of catalytic combustion [2,3]. Some hexaaluminate compounds have been proposed as heat-resistant catalysts [4–6], whereas noble-metal catalysts are the most active as ignition catalysts [7,8]. Supported metals play an important role in the field of heterogeneous catalysis including oxidation reactions. Their performance is strictly related to the nature of the support through dispersion of the metal and metal–support interaction effects. The purpose of the present study is to investigate low-temperature ignition activity of palladium catalysts, which has been known as the most active material for methane oxidation, supported on $Al_2O_3$–transition-metal oxides. In-situ XRD and temperature-programmed desorption (TPD) of oxygen were employed

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to evaluate the effect of the support. The relation between the catalytic activity and the physical and chemical properties of palladium particles supported on mixed oxides were also discussed.

## 2. Experimental

Mixed oxide supports ($Al_2O_3$–$MO_x$; M=Co, Cr, Cu, Fe, Mn, and Ni) were prepared from a mixed aqueous nitrate solution of aluminum and transition metals. The resultant precursor was dried and calcined at 800°C for 5 h in air. Palladium was introduced by impregnation of a support oxide with a $Pd(NO_3)_2$ solution. The impregnated powders were calcined at 800°C for 5 h; the final catalyst contained 1.1 wt% palladium.

The catalytic experiments have been performed using a conventional flow reactor at atmospheric pressure. The gaseous mixture of methane (1 vol %) and air (99 vol%) was supplied to the reactor at a space velocity of 48 000 $h^{-1}$. The methane conversion in the effluent gas was analyzed by on-line gas chromatography. The column used for separation of $CH_4$, $CO_2$ and air was Porapak Q and that for separation of $N_2$, $O_2$, $CH_4$, and CO was MS-4A. The crystalline phase and surface area of the catalysts were determined by XRD (RIGAKU, RINT-1400) and by BET with nitrogen as the adsorbate, respectively. Supported palladium particles and their size were observed by TEM (JEOL, JEM-2000FX).

In-situ XRD was employed for establishing the crystalline phases of palladium species on the support at high temperatures. Palladium was completely oxidized in an oxygen flow prior to the measurement. The XRD was carried out after holding for 30 min at each temperature until PdO was decomposed.

Temperature-programmed desorption (TPD) of oxygen was measured in a flow system. The sample was reduced in an He stream (50 ml $min^{-1}$) at 800°C and subsequently cooled to room temperature. Thereafter, the adsorption of oxygen on the sample was performed in an $O_2$ stream of 50 ml $min^{-1}$ at the desired temperature for 2 h, then followed by cooling to room temperature. The sample was heated at a constant rate (5°C $min^{-1}$) in an He stream (50 ml $min^{-1}$), and the desorbed oxygen monitored by a TCD cell.

## 3. Results and discussion

Activities and surface areas of Pd catalysts supported on $Al_2O_3$-based mixed oxide (Pd/$Al_2O_3$–$MO_x$; M=Co, Cr, Cu, Fe, Mn, and Ni) are summarized in Fig. 1. In the case of Pd/$Al_2O_3$, the conversion of methane reached 10% at 365°C and steeply increased until complete oxidation was achieved. Addition of transition metals significantly reduced the surface areas. Also, catalytic activities deteriorated with these additives, except for M=Co and Ni. The catalysts, added with Co and Ni, exhibited almost the same activity as that of Pd/$Al_2O_3$ in the low-temperature range in spite of their low surface areas. To elucidate the effects of these additives, palladium catalysts supported on the mixed oxides with different compositions were prepared and characterized.

Fig. 2 summarizes the catalytic activity of Pd/$mAl_2O_3$–$nCo_3O_4$. The surface area decreased monotonously with increasing Co content of the support. The catalysts with low Co contents demonstrated almost the same activity as that of Pd/$Al_2O_3$ at reaction temperatures below 400°C. However, the increase of the Co content of the support deteriorated the activity. As can be seen from Fig. 2, the catalytic activity of the supported Pd was strongly dependent on the Co content. After initiation of the reaction, the conversion increased up to ca. 700°C for the catalysts with small Co contents. However, for the Co-rich

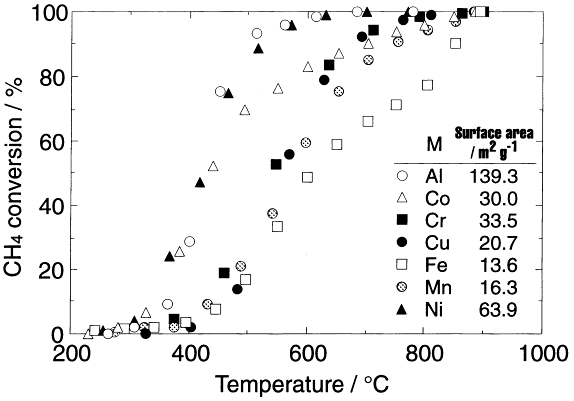
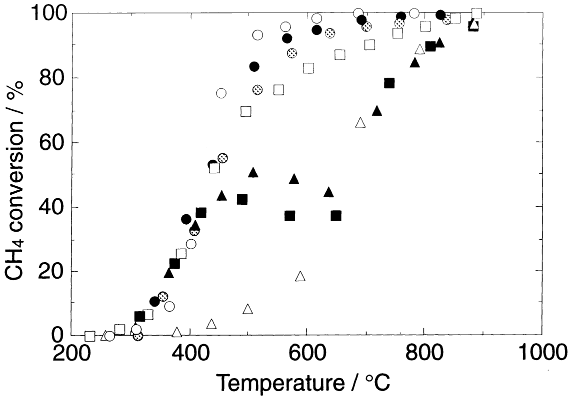


Fig. 1. Catalytic combustion of methane over 1.1 wt% Pd/$Al_2O_3$–$MO_x$ (M=Co, Cr, Cu, Fe, Mn, and Ni) catalysts. Reaction conditions: $CH_4$, 1 vol%; air, 99 vol%; and S.V., 48 000 $h^{-1}$.



| | Catalyst | Surface area / $m^2$ $g^{-1}$ |
|---|---|---|
| ○ | $Al_2O_3$ | 139.3 |
| ⊗ | $6Al_2O_3$-$Co_3O_4$ | 81.5 |
| ● | $3Al_2O_3$-$Co_3O_4$ | 47.6 |
| □ | $3Al_2O_3$-$2Co_3O_4$ | 30.0 |
| ▲ | $3Al_2O_3$-$4Co_3O_4$ | 13.7 |
| ■ | $3Al_2O_3$-$8Co_3O_4$ | 5.1 |
| △ | $Al_2O_3$-$12Co_3O_4$ | 1.8 |

Fig. 2. Catalytic combustion of methane over 1.1 wt% Pd/$m$$Al_2O_3$–$n$$Co_3O_4$ catalysts. Reaction conditions: $CH_4$, 1 vol%; air, 99 vol%; and S.V., 48 000 $h^{-1}$.

catalysts, the activity decreased with a rise in reaction temperature between ca. 500° and 700°C. This drop in activity was observed for the catalysts with Co/Al=2 and 4.

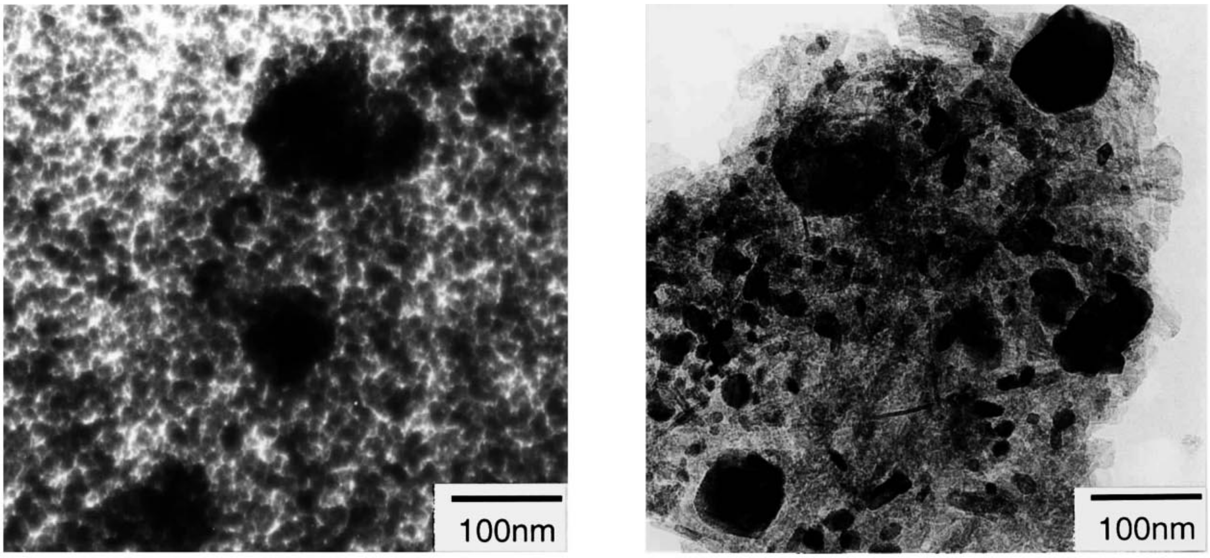
The decrease in surface area with increasing additive was also observed for the series of Pd/$m$$Al_2O_3$–$n$NiO catalysts (Table 1). However, the catalytic activity increased continuously with the nickel content, irrespective of the lower surface area, and the maximum activity was obtained at the composition of Pd/$Al_2O_3$–36NiO. The Pd/NiO catalyst exhibited both, the lowest surface area and the lowest activity in the series of Pd/$m$$Al_2O_3$–$n$NiO. Although the large surface area plays an important role in promoting the overall activity in relation to a high dispersion of active Pd, this parameter was not directly reflected in the activity in the present series.

Transmission electron microscopy (TEM) was employed for observation of the palladium species within the $m$$Al_2O_3$–$n$NiO supports (Fig. 3) To obtain particle size distributions of palladium, 100 Pd particles were observed. It is expected that palladium particles form agglomerates more easily on the support with a small surface area. However, the observed Pd particles on the $m$$Al_2O_3$–$n$NiO support were very fine and uniformly distributed as compared with those on the $Al_2O_3$ support, as shown in Fig. 3. The mean particle size of palladium is summarized in Table 1. The average size of the Pd particles observed on $m$$Al_2O_3$–$n$NiO was smaller than that on $Al_2O_3$. Pd particles were unobservable at a high concentration of Ni in the support because of strong absorption and/or scattering of the incident electron beam by Ni atoms. Therefore, the X-ray line broadening method was

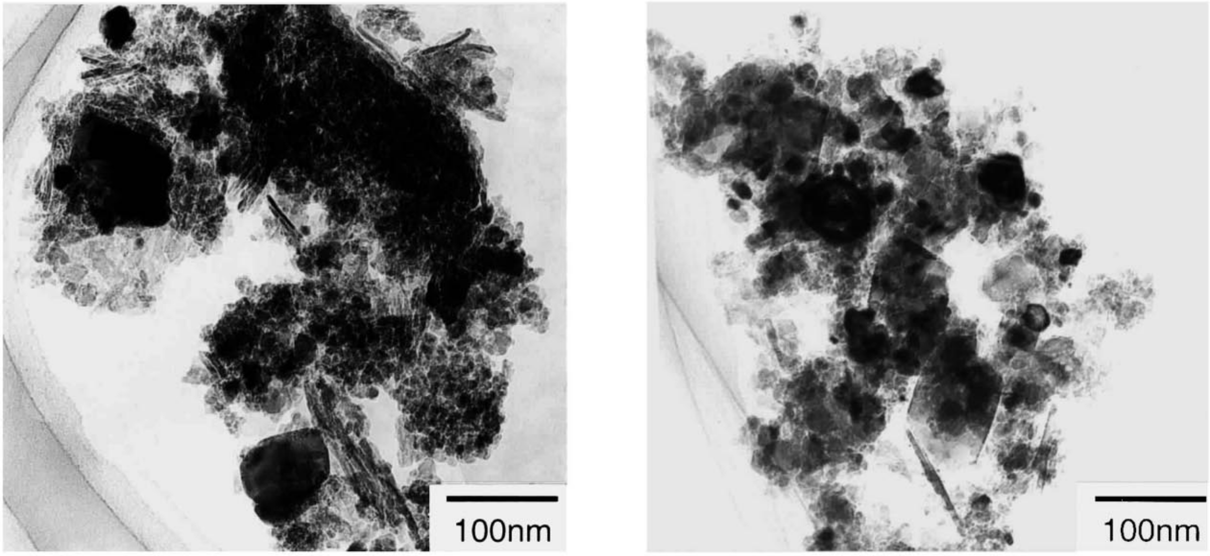
Table 1
Surface areas, catalytic activities, and sizes of palladium particles of 1.1 wt% Pd/$m$$Al_2O_3$–$n$NiO

| Catalyst | Surface area [a] ($m^2$ $g^{-1}$) | Catalytic activity [b] (°C) | | | Crystal size of palladium (nm) | |
|---|---|---|---|---|---|---|
| | | $T$10 | $T$30 | $T$90 | | |
| Pd/$Al_2O_3$ | 139.3 | 365 | 400 | 495 | 52.6 [c] | 43.1 [d] |
| Pd/9$Al_2O_3$–NiO | 150.5 | 340 | 380 | 480 | 37.3 | 32.5 |
| Pd/9$Al_2O_3$–2NiO | 107.4 | 340 | 380 | 525 | 38.1 | 39.0 |
| Pd/$Al_2O_3$–2NiO | 63.9 | 330 | 375 | 520 | 35.7 | 20.5 |
| Pd/$Al_2O_3$–8NiO | 40.3 | 315 | 380 | 540 | 39.0 | — |
| Pd/$Al_2O_3$–18NiO | 21.9 | 315 | 375 | 465 | 34.2 | — |
| Pd/$Al_2O_3$–36NiO | 13.6 | 310 | 350 | 460 | 32.0 | — |
| Pd/NiO | 1.7 | 410 | 475 | 640 | 52.8 | — |

[a] Measured by BET method.
[b] Temperatures at which methane conversion levels are 10, 30 and 90%, respectively.
[c] Estimated from PdO(101) by Scherrer's equation.
[d] Mean particle size obtained from TEM observation.



$Pd/Al_2O_3$ $Pd/9Al_2O_3$-NiO



$Pd/9Al_2O_3$-2NiO $Pd/Al_2O_3$-2NiO

Fig. 3. TEM photographs of 1.1 wt% Pd/$m$$Al_2O_3$–$n$NiO catalysts.

employed to estimate the particle size of palladium. Since palladium was dispersed in the oxidized state, i.e. PdO, the crystalline size of PdO was estimated by analyzing the width of the diffraction line of PdO(101) by Scherrer's equation. As shown in Table 1, the mean particle size of palladium observed by TEM was comparable with the PdO crystallite size estimated from XRD. Therefore, it can be assumed that the mean particle size of PdO can be estimated by the line broadening analysis even for the support with high

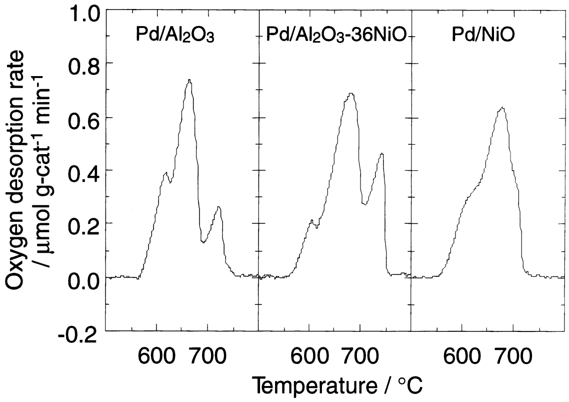


Fig. 4. TPD profiles of oxygen from 1.1 wt% Pd/$m$Al$_2$O$_3$–$n$NiO catalysts. Heating rate, 5°C min$^{-1}$. Samples were heated in oxygen stream (O$_2$, 50 ml min$^{-1}$) at 500°C for 2 h, followed by cooling to room temperature prior to the measurement.

content of Ni. As shown in Table 1, it can be deduced that the small grain size of PdO leads to a high catalytic activity despite the low surface area of the support. In the most active Pd/Al$_2$O$_3$–36NiO, the grain size of PdO was the smallest in this catalyst system.

Although Ni addition in the support plays an important role to enhance the catalytic activity by maintaining the high dispersion of the palladium particles, it is likely that other chemical effects also affect the activity. Temperature-programmed desorption (TPD) of oxygen was employed to elucidate the reduction–oxidation properties of supported Pd. Fig. 4 shows TPD profiles of oxygen from Pd/Al$_2$O$_3$, Pd/NiO, and Pd/Al$_2$O$_3$–36NiO. Every support without active Pd species hardly exhibited oxygen desorption. Therefore, all desorption peaks are ascribed to the desorption from Pd. In Pd/Al$_2$O$_3$, three distinct peaks were observed at ca. 600°, 660°, and 720°C. These peaks reflect the different adsorption states of oxygen on palladium. No desorption peak was observed above 750°C because of complete decomposition of PdO to Pd. The peak temperature at ca. 660°C precisely agreed with the thermodynamic dissociation of bulk PdO [9,10]. Although three different adsorption states of oxygen were observed in Pd/Al$_2$O$_3$–36NiO, as McCarty [11] reported for the stable oxide species (PdO$_x$), the sequence of intensities of these desorption peaks were changed and shifted to the high-temperature side. Pd/NiO has shown a single desorption peak centered at ca. 660°C with two shoulders at both sides. A small amount of desorbed oxygen with Pd/NiO is probable because of partial inclusion of metallic Pd even after O$_2$ adsorption due to the large particle size.

Most studies have shown that TPD curves are sensitive to the kind of support, the dispersion of active palladium species, and the presence of promoters. Thus, even for catalysts with the same metal and similar dispersion and weight loading, significant differences are observed in TPD curves for different supports [12].

Adsorption of oxygen species was further investigated by TPD after various pretreatments. Fig. 5 shows TPD profiles of oxygen after preadsorption of oxygen on Pd/Al$_2$O$_3$–36NiO at different temperatures. The low-temperature desorption peak ca. 600°C decreased gradually with rising temperature. Oxygen preadsorption at high temperature promoted strong oxygen adsorption. The total amounts of oxygen desorption with different pretreatment conditions are summarized in Table 2. It is revealed that oxygen desorption from Pd/Al$_2$O$_3$–36NiO was larger than that from Pd/Al$_2$O$_3$ in every case. The amount of desorption from Pd/NiO was extremely small after preadsorption below 500°C. The sequence of oxygen uptake at 500°C is Pd/Al$_2$O$_3$–36NiO>Pd/Al$_2$O$_3$>Pd/NiO. These results indicate that the active catalyst adsorbs oxygen at lower temperatures.

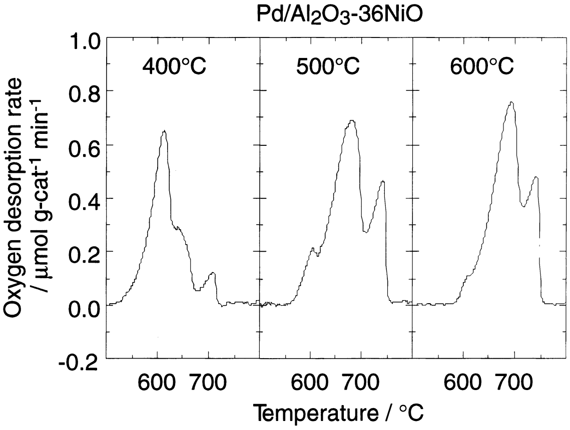


Fig. 5. TPD profiles of oxygen from 1.1 wt% Pd/$m$Al$_2$O$_3$–$n$NiO catalysts. Heating rate, 5°C min$^{-1}$. Samples were heated in oxygen stream (50 ml min$^{-1}$) at the indicated temperatures for 2 h, which was followed by cooling to room temperature prior to the measurement.

Table 2
Amount of desorbed oxygen from 1.1 wt% Pd/$m$Al$_2$O$_3$–$n$NiO catalysts

| Pretreatment temperature (°C) | Amount of desorbed oxygen (μmol g cat$^{-1}$) | | |
|---|---|---|---|
| | Pd/Al$_2$O$_3$ | Pd/Al$_2$O$_3$–36NiO | Pd/NiO |
| 300 | 12 | 17 | 7 |
| 400 | 18 | 23 | 14 |
| 450 | 22 | 28 | 13 |
| 500 | 29 | 34 | 28 |
| 600 | 32 | 33 | 35 |
| 700 | 25 | 38 | 37 |
| 800 | 28 | 29 | 34 |

Theoretical value when PdO is completely reduced to Pd is 39 μmol g cat$^{-1}$.

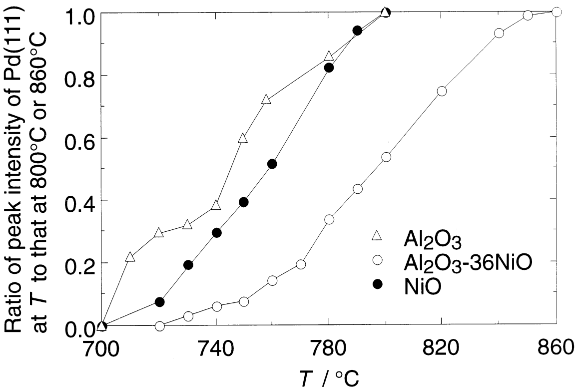


Fig. 7. Relative peak intensity of Pd metal of 1.1 wt% Pd/$m$Al$_2$O$_3$-$n$NiO catalysts at various temperature.

TPD measurement indicated that palladium supported on Al$_2$O$_3$–36NiO was kept in a high oxidation state as compared to that on the other support. In-situ X-ray diffraction was employed to observe the PdO phase on $m$Al$_2$O$_3$–$n$NiO. Fig. 6 shows typical in-situ XRD patterns of Pd/Al$_2$O$_3$ over the temperature range from 700° to 800°C in He. The PdO line was weakened with increasing temperature, which was accompanied with a change to Pd metal. PdO was completely reduced to Pd metal at 800°C. The constant width of the diffraction lines of PdO and Pd indicated that redispersion and/or aggregation of palladium particles did not occur significantly during heat treatment. The relative intensities of the metallic Pd (111) diffraction line of Pd/$m$Al$_2$O$_3$–$n$NiO catalysts are summarized in Fig. 7, in which decomposition to metallic Pd is complete at 800°C or 860°C. Dissociation of PdO on Al$_2$O$_3$ and NiO initiated at 700°C, and both catalysts exhibited almost the same transformation temperature to the metallic phase, whereas PdO was more stable on Al$_2$O$_3$–36NiO support than on other supports. The addition of NiO to Al$_2$O$_3$ appears to suppress the dissociation of PdO, thus resulting in high catalytic activity.

## 4. Conclusions

Pd catalysts supported on Al$_2$O$_3$-based mixed oxides system were investigated as ignition catalysts for methane oxidation. Pd/$m$Al$_2$O$_3$–$n$NiO catalysts

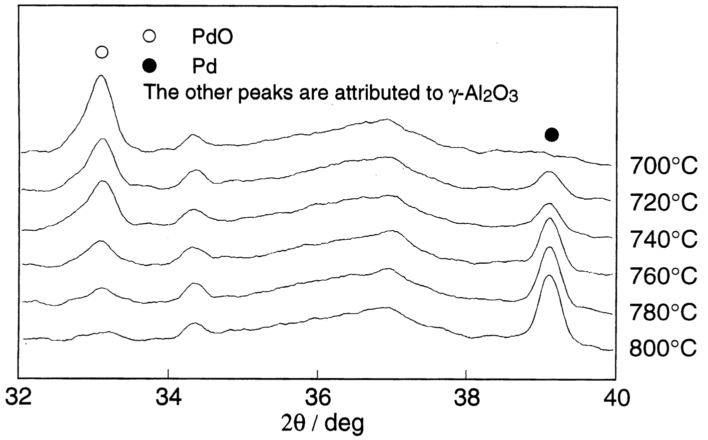


Fig. 6. In-situ XRD patterns of 1.1 wt% Pd/Al$_2$O$_3$ catalyst.

showed excellent catalytic activity. The activity was enhanced with an increase of NiO content of the support despite its lower surface area. Particle size of palladium tended to decrease with increasing Ni content in the support. Pd/$Al_2O_3$–36NiO with fine dispersion of palladium particles demonstrated excellent activity. TPD of oxygen revealed that the reduction–oxidation properties of palladium are enhanced by employing $Al_2O_3$–36NiO as a support. Oxygen adsorption at low temperatures is one of the important parameters to determine the activity. In-situ XRD indicated that $Al_2O_3$–36NiO support suppressed the thermal dissociation of active palladium species, PdO. The stability of the PdO species at higher temperatures is suggested to directly correspond to the increase in catalytic activity.

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