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Property of Pd-supported catalysts for catalytic combustion

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Abstract

The catalytic properties of Pd/$Sr_{0.8}La_{0.2}XAl_{11}O_{19}$ (X = Al and Mn) and Pd/Al_2O_3–MO_x (M = Co, Cr, Cu, Fe, Mn and Ni) catalysts were investigated for use in catalytic combustion. The activity of Pd/$Sr_{0.8}La_{0.2}Al_{12}O_{19}$ initially increased with rise in temperature, but decreased at high temperatures (ca. 700°C). The drop in catalytic activity was steep when the supported Pd particles were sintered after calcination above 1000°C. The activity drop accompanied dissociation of PdO into metallic Pd. Such significant drop in catalytic activity can be avoided by the use of Mn-substituted hexaaluminate (X = Mn) as a catalyst support, due to its activity for combustion. The drop could be also avoided by use of Pd/Al_2O_3–NiO catalysts calcined at low temperatures. Although the surface area decreased with increasing NiO content, the catalytic activity increased. Pd particle size is an important factor in determining catalytic activity.

Keywords: Palladium-supported catalysts; Catalytic combustion

1. Introduction

In recent investigations, the use of oxidation catalysts in a catalytic combustor has played an important role in reducing nitrogen oxide emission [1]. A maximum temperature in a conventional flame combustion above 1500°C can be reduced to ca. 1300°C by use of catalytically stabilized fuel–lean combustion, in which thermal NO_x formation is negligible. The key to this technology, therefore, is the development of improved catalyst performances involving, e.g., high thermal stability above 1200°C and high catalytic activity at low temperature. Partial substitution of transition metals such as Mn for Al significantly promotes catalytic reaction due to high reduction–oxidation activity of substituent species without destroying high thermal stability. Some Mn-substituted hexaaluminate compounds exhibit excellent thermal stability and catalytic activity, so that they are expected to be the most promising combustor catalyst materials [2–4]. On the other hand, the catalytic combustor also requires a ignition catalyst which possesses higher catalytic activity to initiate the surface reaction at low temperatures. Many researchers have paid attention to development of precious metal catalysts, in particular palladium, which shows excellent activity for the methane combustion. In this study, the catalytic activity of supported palladium was investigated for combustion of methane. Temperature depen-

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dence of catalytic activity and its relation with the dispersion and chemical state of palladium were discussed.

2. Experimental

Pd/hexaaluminate catalysts were prepared by two methods. Pure 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. A solution of tetramine palladium dichloride was added during the hydrolysis (method A). In a second preparation method, the support precursor was dried and calcined at 1200°C in air and palladium was deposited by impregnation of $Pd(NO_3)_2$ (method B). Both samples were calcined at 1000°C or 1200°C in air.

Mixed oxide supports (Al_2O_3–MO_X; M = Co, Cr, Cu, Fe, Mn and Ni) were prepared by two preparation methods: transition metal oxide deposition on γ-alumina by impregnation (method C) or mixed aqueous solution of aluminum and transition metal nitrate decomposition (method D). The precursor was dried and calcined at 800°C in air. Palladium was deposited by impregnation of $Pd(NO_3)_2$ prior to calcination at 800°C in air.

In situ XRD was carried out to observe the crystalline phases of palladium species. TEM was used for the observation of supported palladium particles and of particle size distribution of palladium. Temperature-programmed desorption of oxygen (TPD) was measured in a flow system. The sample oxidized in advance was heated in a helium stream (50 ml min^{-1}). Reoxidation profiles (TPRO) were obtained in He containing 5 vol% O_2 (same rate) following TPD measurement. Catalytic combustion of methane over supported palladium catalysts was examined in a conventional flow reactor at atmospheric pressure. A gaseous mixture of CH_4 (1 vol%), O_2 (20 vol%), and N_2 (balance) was supplied at a space velocity of 48000 h^{-1}. Methane conversion in the effluent gas was analyzed by on-line gas chromatography.

3. Results and discussion

3.1. Catalytic combustion of methane over Pd/hexaaluminate

The catalytic activities of Pd/SLA and Pd/SLMA catalysts prepared from each route are shown in Figs. 1 and 2, respectively. TEM showed that the calcination at elevated temperatures caused a significant grain growth of palladium particles. Catalytic activities of Pd/SLA and Pd/SLMA prepared from method A increased with increasing heat treatment. The conversion steadily increased with rising temperature except for Pd/SLA calcined at 1200°C. Pd/SLA showed a decrease forming a minimum between ca. 700°C and ca. 850°C.

An enhancement of catalytic activity at lower temperature was achieved over Pd/SLA made by method B. However, the activity drop was also observed and was more obvious for the sample with the higher calcination temperature. Support material, SLA, possessed poor catalytic activity and led to a higher initiation temperature and a steep rise in methane conversion.

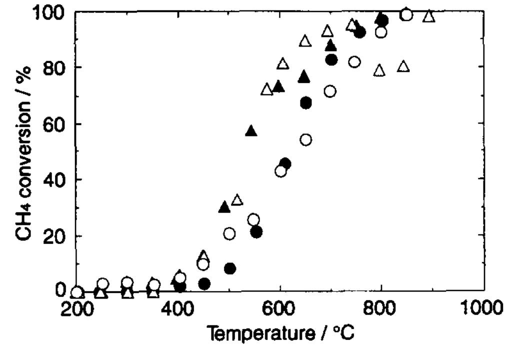

Fig. 1. Catalytic combustion of methane over 1.44 wt.% $Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}$ (open symbol) and 1.44 wt.% $Pd/Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (closed symbol) prepared by method A. Calcination temperature: (○) 1000 and (△) 1200°C. Reaction conditions: CH_4, 1 vol.%; O_2, 20 vol.%; N_2, balance; space velocity, 48000h^{-1}.

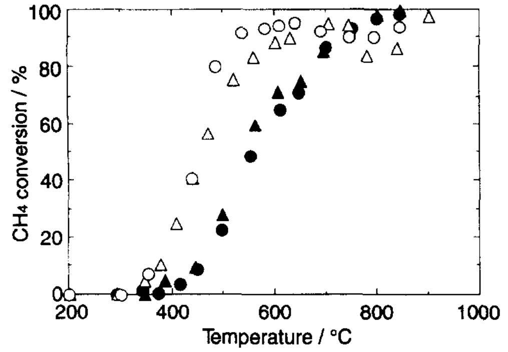

Fig. 2. Catalytic combustion of methane over 1.44 wt.% $\mathrm{Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}}$ (open symbol) and 1.44 wt.% $\mathrm{Pd/Sr_{0.8}La_{0.2}MnAl_{11}O_{19}}$ (closed symbol) prepared by method B. Calcination temperature: (○) 1000 and (△) 1200°C. Reaction conditions are the same as in Fig. 1.

This drop, therefore, is related to the nature and size of palladium. This phenomenon is also observed for other supported palladium catalysts, such as Pd/alumina [5]. On the other hand, two Pd/SLMA catalysts prepared by the different routes exhibited almost the same activity and the most promising effect was the absence of the drop of methane conversion in the high temperature region. Thus complete combustion could be achieved at lower temperatures as compared with the Pd/SLA catalysts.

3.2. In situ X-ray analysis of Pd species

To observe catalytic behavior in the high temperature region, the temperature dependence of activity over Pd/SLA was measured (Fig. 3). Catalytic activity steadily increased with rising temperature up to ca. 700°C. The slope of the conversion curve became negative from 780°C to 830°C, but complete oxidation of methane was achieved at 900°C. During the cooling process, the catalytic activity significantly decreased to ca. 30% at 800°C exhibiting obvious hysteresis. The activity increased again from 800°C to recover the same conversion level at 700°C as observed in the heating process. Thus, in situ X-ray diffraction was employed to qualitatively analyze the Pd species under catalytic reaction conditions. The intensity of the Pd line changed with temperature, whereas no appreciable change was observed for the diffraction pattern of hexaaluminate. Fig. 4 shows 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 consisted of unresolved lines from metallic Pd and PdO. The intensity of the Pd line, which gradually de-

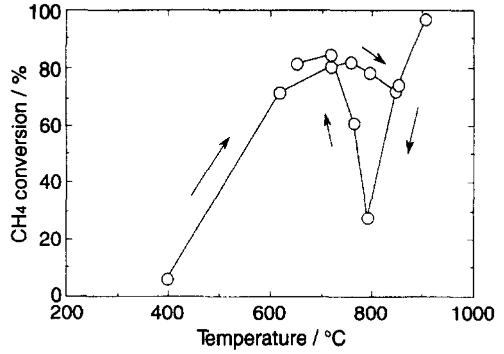

Fig. 3. Catalytic combustion of methane over 1.44 wt.% $\mathrm{Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}}$ calcined at 1200°C. Reaction conditions are the same as in Fig. 1.

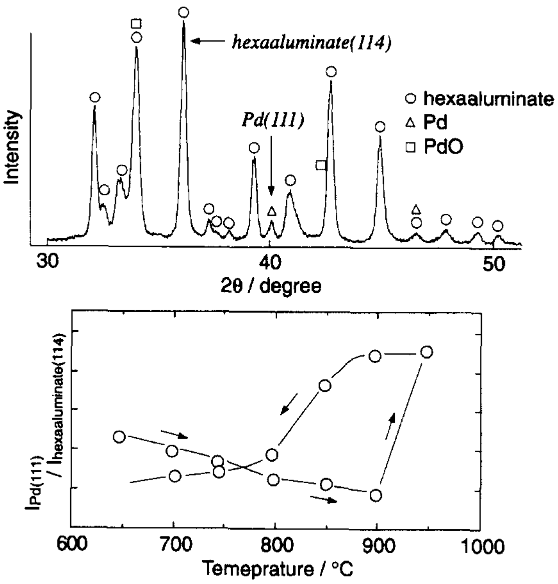

Fig. 4. X-ray diffraction pattern of 1.44 wt.% $\mathrm{Pd/Sr_{0.8}La_{0.2}Al_{12}O_{19}}$ calcined at 1200°C, and change in relative peak intensity of Pd with heating and cooling treatment in a stream of gas mixture of CH4 (1 vol.%) and air (99 vol.%).

creased with a rise in temperature up to 900°C, showed a drastic increase above 900°C. When the sample was cooled to ca. 700°C, the intensity of the diffraction line dropped to the original intensity. These results indicate that the change of the chemical state of palladium, from PdO to Pd, is the key to an explanation of the complicated catalytic behavior at high temperatures.

3.3. Catalytic activity of Pd/Mn-substituted hexaaluminate

As shown above the activity drop was avoided by using SLMA as a support material independent of preparation method. The activity of Pd/SLMA differs from that of Pd/SLA because of the reduction–oxidation cycle of Mn in the hexaaluminate lattice. Although SLMA has intrinsically low activity, much lower than that of Pd at low temperatures, their activities became comparable around the temperature at which methane conversion becomes negative over Pd/SLA. This leads to parallel catalytic reactions over Pd and SLMA. Fig. 5 compares TPD/TPRO profiles of Pd/SLA, Pd/SLMA and SLMA. Mn in the hexaaluminate lattice generates reversible oxygen desorption due to reduction/oxidation between Mn^{2+} and Mn^{3+}. The desorption and uptake of oxygen appeared in the TPD and TPRO profiles of Pd/SLMA amounted to the sum of oxygen desorbed and taken up for Pd/SLA and SLMA. In this situation, the activity drop due to Pd species can be compensated by the catalytic reaction over SLMA support. The use of catalytically active support materials such as SLMA is a possible way to overcome the unstable catalytic activity of the supported palladium catalyst.

3.4. Catalytic combustion of methane over Pd/Al_2O_3–MO_x (M = Co, Cr, Cu, Fe, Mn and Ni)

Other support materials were investigated to further improve catalytic activity. Figs. 6 and 7 summarize the surface area and catalytic activ-

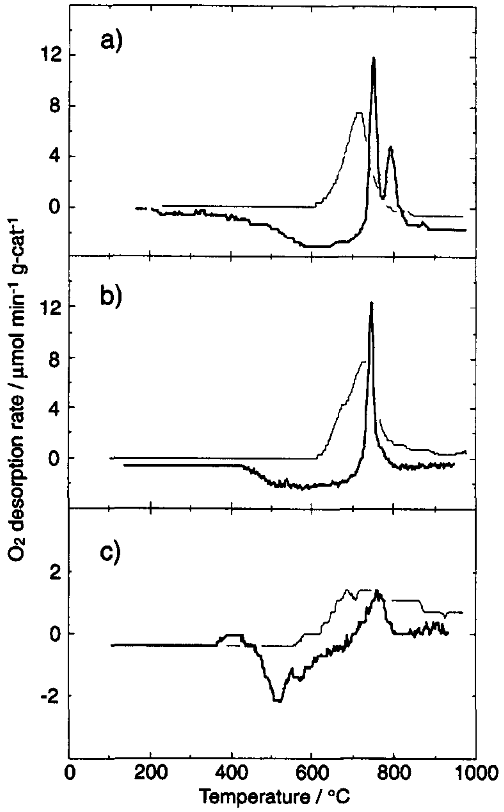

Fig. 5. TPD (hair line) and TPRO (thick line) profiles of (a) 1.44 wt.% Pd/$Sr_{0.8}La_{0.2}Al_{12}O_{19}$ (Pd/SLA), (b) 1.44 wt.% Pd/$Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (Pd/SLMA) and (c) $Sr_{0.8}La_{0.2}$-$MnAl_{11}O_{19}$ (SLMA). Each sample was calcined at 1200°C in advance.

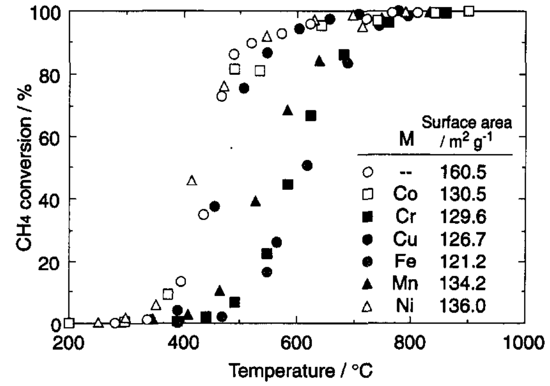

Fig. 6. Catalytic combustion of methane over 1.1 wt.% Pd/Al_2O_3-MO_x (M = Co, Cr, Cu, Fe, Mn and Ni) prepared by method C calcined at 800°C. Reaction conditions are the same as in Fig. 1.

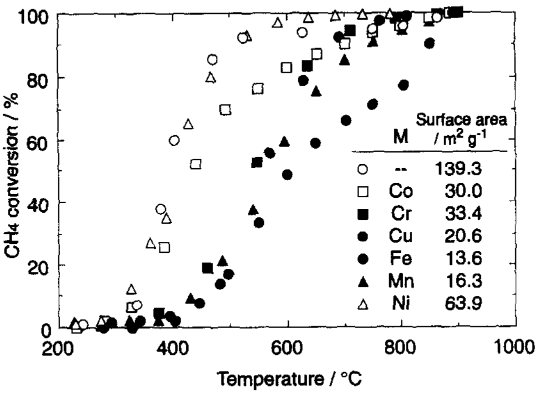

Fig. 7. Catalytic combustion of methane over 1.1 wt.% $Pd/Al_2O_3-MO_x$ (M = Co, Cr, Cu, Fe, Mn and Ni) prepared by method D calcined at 800°C. Reaction conditions are the same as in Fig. 1.

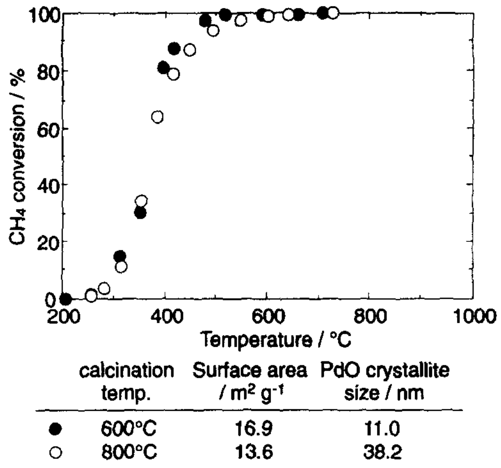

Fig. 8. Catalytic combustion of methane over 1.1 wt.% $Pd/Al_2O_3-36NiO$ calcined at 600°C and 800°C. Reaction conditions are the same as in Fig. 1.

ity for methane combustion over $Pd/Al_2O_3-MO_x$ (M = Co, Cr, Cu, Fe, Mn and Ni) catalysts prepared by methods C and D, respectively. In a series of catalysts prepared by method C, the surface area of Pd/Al_2O_3 (160.5 $m^2\ g^{-1}$) slightly decreased by addition of transition metal oxides. The catalytic activity was deteriorated by addition of Cr, Mn and Fe, since the small surface area led to low dispersion of Pd. The addition of transition metal oxide was effective in avoiding unstable catalytic activity in the high temperature region and complete methane oxidation was achieved below 800°C.

On the other hand, the surface area of Pd/Al_2O_3 (139.5 $m^2\ g^{-1}$) was significantly decreased by these additives in a series of catalysts prepared by method D. Catalytic activity was also decreased by the additives except for Ni. The activity drop at high conversions was also not observed in this series.

Only Pd/Al_2O_3-NiO catalysts prepared from both methods demonstrated almost the same conversion as Pd/Al_2O_3, though large particle size of Pd was expected from the smaller surface areas of the support oxides. Since Ni addition gives a good activity, Pd/Al_2O_3-NiO catalysts with different compositions of support were prepared and characterized (Table 1). The n/m ratios in the Pd/mAl_2O_3-nNiO mean the molar ratio between Al_2O_3 and NiO. T10, T30, T70 and T90 in the table are temperatures at which methane conversion level reaches 10, 30, 70 and 90%, respectively. The catalytic activity in-

Table 1
Surface areas and catalytic activities of 1.1 wt.% Pd/mAl_2O_3-nNiO calcined at 800°C

Catalyst	Surface area/ $m^2\ g^{-1}$	Catalytic activity/°C			
		T10	T30	T70	T90
Pd/Al_2O_3	139.3	340	370	420	500
$Pd/9Al_2O_3-NiO$	150.0	340	380	430	480
$Pd/9Al_2O_3-2NiO$	107.4	350	380	430	500
Pd/Al_2O_3-2NiO	63.9	320	370	440	510
Pd/Al_2O_3-8NiO	40.3	320	370	450	540
$Pd/Al_2O_3-18NiO$	21.9	320	370	430	470
$Pd/Al_2O_3-36NiO$	13.6	320	340	400	470
Pd/NiO	2.6	390	480	540	590

creased with increasing concentration of Ni in the support, but the surface area exhibited reverse behavior. The catalytic activity was maximal at the composition of Pd/Al_2O_3–36NiO and decreased at the composition of Pd/NiO in a series of Pd/$m$$Al_2O_3$–$n$NiO. To enhance the catalytic activity, high surface area materials are employed as support to prevent sintering of active species, i.e. palladium. However, the surface area was not directly related with the metal dispersion and catalytic activity in the present system.

It is difficult to observe supported small particles on the support by electron microscopy, because scattering intensity of Ni is too strong to distinguish between palladium and nickel atoms. Mean crystal size of palladium, therefore, was estimated from XRD measurement. Palladium was dispersed in the state of PdO. The size of palladium supported on $m$$Al_2O_3$–$n$NiO was obtained from the diffraction line of PdO(101) by the X-ray line broadening method which has been popularly employed for the particle size of supported palladium species [6,7]. The particle sizes obtained by LBA showed good agreement with the particle sizes measured by TEM analysis at low concentration samples of Ni. The LBA method was employed for the samples with high content of Ni for which TEM observation was impossible. Fig. 8 shows that catalytic activity of 1.1 wt.% Pd/Al_2O_3–36NiO calcined at 600°C and 800°C. The catalytic activity and the surface area decreased and the crystallite size of PdO increased for the sample with higher heat treatment temperature. This demonstrates that particle size of palladium is of fundamental significance for catalytic activity.

Table 2
Crystallite sizes and catalytic activities of 1.1 wt%. Pd/$m$$Al_2O_3$–$n$NiO

Catalyst	PdO crystallite size/nm	T30 [a]/ °C
Pd/Al_2O_3	52.6	370
Pd/Al_2O_3–18NiO	45.5	370
Pd/Al_2O_3–36NiO	38.2	340
Pd/NiO	52.8	480

[a] Temperature at which methane conversion is 30%.

As shown in Table 2, crystals of PdO are highly dispersed on the $m$$Al_2O_3$–$n$NiO support in spite of its low surface area. These results indicate that the unstable catalytic activity in the high temperature region is avoided by using of small palladium particles and a good relation exists between the catalytic activity and PdO crystallite size. Pd/Al_2O_3–36NiO demonstrated excellent activity for catalytic combustion at low temperatures.

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