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Catalysis Today 35 (1997) 197–202

CATALYSIS TODAY

Oxidation of methane over Pd-supported catalysts

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Abstract

Pd catalysts supported on Al_2O_3-based mixed oxides were investigated for catalytic combustion. Pd/$m$$Al_2O_3$-$n$NiO catalysts demonstrated excellent catalytic activity. Although the surface area decreased with increasing NiO content in the support, the catalytic activity increased inversely. Supported Pd was characterized by X-ray line broadening method, XPS, and by temperature programmed desorption (TPD) of oxygen. The core level binding energy (BE) of palladium increased with decreasing crystal size. This particle-size-induced BE shift depended on the crystalline phase of the support. The crystalline phase of the support affected the catalytic activity and the interaction between palladium and the support. Pd/Al_2O_3-36NiO demonstrated excellent activity for catalytic combustion at low temperatures. Pd particle size and support material play important roles in determining catalytic activity.

Keywords: Oxidation; Methane; Pd-supported catalysts

1. Introduction

Catalytic combustion has been regarded as an important technology ever since Davy found combustion without flame over platinum wire [1–3]. High temperature catalytic combustion has two important advantages in its practical applications; high combustion efficiency and reduction of the thermal NO_x emission associated with the conventional flame combustion. Some specific characteristics are requested for the catalysts in practical applications. High thermal stability above 1200°C is requested because high operation temperatures above 1200°C immediately deteriorates most conventional catalysts. Furthermore, the catalysts in the combustor are subjected to a wide range of temperatures. The catalysts, therefore, need to cover different activities and thermal stabilities. Therefore, two types of catalyst materials should be developed for this purpose; one possesses high thermal stability and the other shows high catalytic activity at low temperatures.

Some Mn-substituted hexaaluminate compounds were reported as promising materials due to their excellent thermal stability and catalytic activity [4–6]. However, the catalytic activity of hexaaluminate is generally insufficient as an ignition catalyst. Noble metal catalysts have been shown to be active for combustion of methane. Palladium has been popularly employed as the most active catalyst for methane combustion [7,8]. The sequence of the catalytic activity for methane oxidation has been reported as Pd > Rh > Pt.

In this study, the catalytic activities of palladium catalysts supported on Al_2O_3-transition metal oxides were investigated for the oxidation

PII S0920-5861(96)00128-9

of methane. The relation between catalytic activity, the effect of transition metal additives to the support and chemical states of palladium are discussed.

2. Experimental

Mixed oxide supports, Al_2O_3-MO_x; M = Co, Cr, Cu, Fe, Mn, and Ni, were prepared from aqueous solution of nitrates. A mixed aqueous solution of aluminum and transition metal nitrate was evaporated and the precursor thus obtained 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.TEM (JEOL, JEM-2000FX) was used for the observation of supported palladium particles and their size distribution. XRD (RIGAKU, RINT-1400) measurements were carried out to observe the crystalline phases of palladium species. Core level ($3d_{5/2}$) binding energy of Pd deposited on the support was obtained from XPS (Shimadzu, ESCA850) measurements. 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}). The oxygen in the effluent gas was detected by using a TCD cell. 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 48 000 h^{-1}. Methane conversion in the effluent gas was analyzed by on-line gas chromatography.

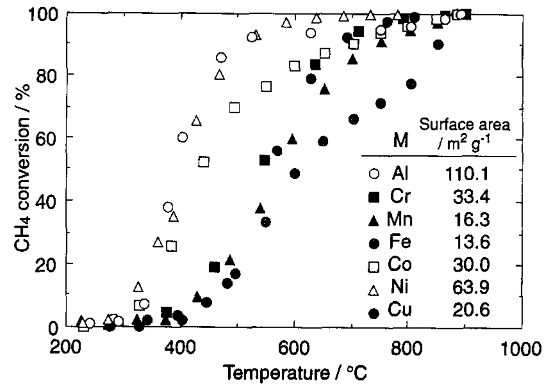

Fig. 1. Catalytic combustion of methane over 1.1 wt% Pd/Al_2O_3-MO_x (M = Co, Cr, Cu, Fe, Mn, and Ni). Reaction conditions; CH_4, 1 vol%; air, 99 vol%; space velocity, 48000 h^{-1}.

3. Results and discussion

Catalytic activity and surface area in a series of Pd/Al_2O_3-MO_x (M = Co, Cr, Cu, Fe, Mn, and Ni) are summarized in Fig. 1. The combustion of methane initiated at ca. 250°C over Pd/Al_2O_3. Then the conversion steeply in-

Table 1

Surface areas, catalytic activity, and PdO crystal sizes of 1.1 wt% Pd/mAl_2O_3-nNiO

Catalyst	Surface area (m^2 g^{-1})	Catalytic activity [a] (°C)			PdO crystal size [b] (nm)	PdO particle size [c] (nm)
		T10	T30	T90		
Pd/Al_2O_3	110.1	340	370	500	52.6	43.1
Pd/Al_2O_3-2NiO	63.9	320	370	510	35.7	20.5
Pd/Al_2O_3-8NiO	40.3	320	370	540	39.0	
Pd/Al_2O_3-18NiO	21.9	320	370	470	34.2	
Pd/Al_2O_3-36NiO	13.6	320	340	470	32.0	
Pd/NiO	2.6	390	480	590	52.8	

[a] Temperatures at which methane conversions are 10, 30, and 90%, respectively. Reaction conditions; CH_4, 1 vol%; air, 99 vol%; space velocity, 48000 h^{-1}.

[b] Estimated by X-ray line broadening method from PdO(101).

[c] Obtained from TEM observation.

creased up to ca. 500°C, but the rise in conversion became gradual between 700 and 850°C. The extremely slow increase of the conversion in high conversion region is characterized by a mass transfer limitation and unique catalytic behavior of the Pd catalyst, accompanied by the oxide–metal transition. This complicated behavior inhibited the complete conversion and sometimes causes a serious problem in using supported Pd catalyst for the catalytic combustion reaction. The surface area of Pd/Al_2O_3 (110.1 m^2 g^{-1}) was seriously lowered with the addition of transition metals. Catalytic activity also deteriorated with these additives, except for Ni and Co. For Pd/Al_2O_3-Fe_2O_3, a gas-phase reaction was observed in the high temperature region, which can be characterized by the steep rise in methane conversion (80–100%) after the plateau in the 50–80% conversion range. The combustion over the NiO-added catalyst initiated at 250°C and demonstrated almost the same activity as Pd/Al_2O_3 in the low temperature region, in spite of the low surface area. Complete combustion over Pd/Al_2O_3-2NiO could be achieved at lower temperatures than with Pd/Al_2O_3. Therefore, supported palladium catalysts with different compositions of Ni were prepared and investigated.

Table 1 summarizes the surface area and catalytic activity in a series of Pd/$m$$Al_2O_3$-$n$NiO. T10, T30, and T90 values in the table are the temperatures at which the methane conversion level is 10, 30, and 90%, respectively. Although the surface area of Pd/$m$$Al_2O_3$-$n$NiO decreased with increasing NiO content, catalytic activity increased inversely and became maximum at the composition of Pd/Al_2O_3-36NiO. The catalytic activity decreased with a further increase in NiO content at Pd/NiO. One important factor in enhancing the catalytic activity is to maintain the large active surface and/or fine microstructure of active palladium species. It appears that the large support surface leads to high dispersion of Pd. But this is not the case in the present Pd/$m$$Al_2O_3$-$n$NiO.

Transmission electron microscopy (TEM) was used to observe the palladium on the $m$$Al_2O_3$-$n$NiO supports. To obtain particle size distributions of palladium, 100 Pd particles were observed. However, TEM observation of palladium particles on the support was difficult when the Ni content in the support increased, because of the strong absorption and/or scattering of the incident beam by Ni atoms in the support. Therefore, an X-ray line broadening method was employed to estimate the particle size of Pd. Different crystalline phases were observed with increasing NiO content in the support (Fig. 2). Alumina was the sole support phase in Pd/Al_2O_3, though its crystallinity was quite low. $NiAl_2O_4$ phase became dominant with an increase in NiO content up to the stoichiometric composition of the spinel (Pd/Al_2O_3-2NiO). The intensity of NiO increased monotonously with a rise in concentration of Ni, and only NiO was contained as the support phase in Pd/NiO.

The XRD patterns indicated that the palladium particles were dispersed in the oxidized

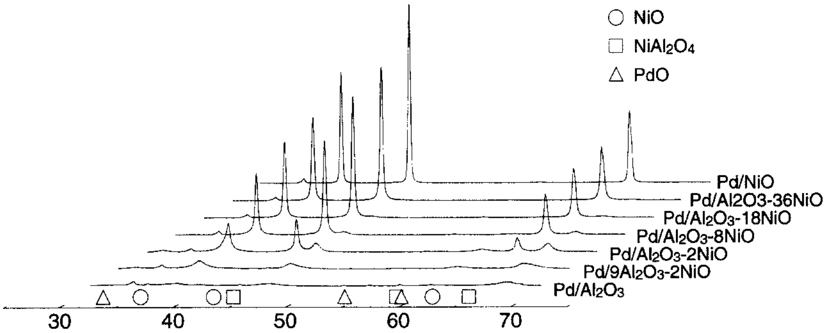

Fig. 2. X-ray diffraction patterns of 1.1 wt% Pd/$m$$Al_2O_3$-$n$NiO calcined at 800°C.

state, i.e. PdO, in the series of catalysts. The mean crystallite size of palladium supported on mAl$_2$O$_3$-nNiO was estimated from the width of the diffraction line of PdO(101) ($2\theta = 33.9°$). The estimation of the particle size was obtained from the peak separation between PdO(101) and PdO(002) and removal of Kα line before fitting to Scherrer's equation. Mean particle sizes obtained from TEM observation were compared with PdO crystal size at the composition of Pd/Al$_2$O$_3$ and Pd/Al$_2$O$_3$-2NiO. Both sizes decreased with Ni addition in the support. Therefore, this estimation was assumed to be valid for the samples with high content of Ni, for which TEM observation was impossible. It is roughly shown that the small grain size of PdO gave rise to high catalytic activity (Table 1).XPS was employed to investigate the chemical state of palladium. The 3d spectra of Pd deposited on the support are shown in Fig. 3. The correction of the energy was made by using the C1s line (284.3 eV). The Pd3d doublet exhibits narrow and symmetric peaks for Pd/Al$_2$O$_3$. The binding energies indicate that palladium particles are in the divalent state, which is supported by the result obtained from XRD measurements. The strong influence of the NiO in the support has been detected. The Pd3d doublet shifted to higher binding energy with increasing of NiO content The highest binding energy was obtained for Pd/Al$_2$O$_3$-36NiO which had the smallest grain size of PdO. Several investigations on metal clusters were reported the particle-size-dependent shifts in the metal core level binding energies in relation to the metal–non-metal transition; direct shifts of the spectral features at the Fermi energy have also been reported for small Pd clusters [9].

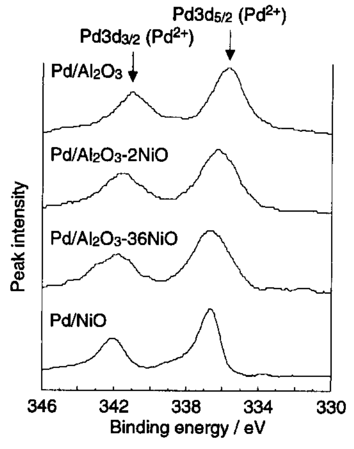

Fig. 3. XPS spectra of Pd3d from 1.1 wt% Pd/mAl$_2$O$_3$-nNiO.

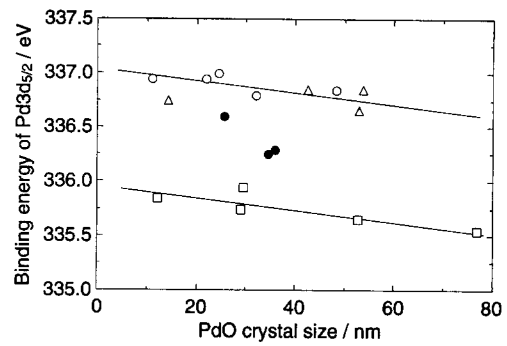

Fig. 4. Dependence of the binding energy of Pd3d$_{5/2}$ on PdO crystal size with different supports; (△) NiO, (○) mAl$_2$O$_3$-nNiO without NiAl$_2$O$_4$ phase, (●) mAl$_2$O$_3$-nNiO with NiAl$_2$O$_4$, and (□) Al$_2$O$_3$.

Three phases were contained in the support depending on the composition; amorphous-like alumina, NiAl$_2$O$_4$ spinel, and NiO. Therefore, samples were classified into four groups by the support and crystal phase, that is, Al$_2$O$_3$, mAl$_2$O$_3$-nNiO with NiAl$_2$O$_4$ phase, mAl$_2$O$_3$-nNiO without spinel phase, and NiO. Samples with different particle size of PdO and/or different crystal phase of support were prepared for the evaluation of the Binding energy. The core level (Pd3d$_{5/2}$) binding energies of Pd are plotted against particle size in Fig. 4. Although the binding energies are scattered between the samples in different groups, it was found to decrease with increasing particle size of PdO within each group. It is demonstrated that the binding energy is strongly affected by the support crystal phase.

To elucidate the relation between catalytic activity and the phases in the support of the Pd catalysts, the reduction–oxidation property was studied by TPD of oxygen. Fig. 5 shows TPD profiles from Pd/mAl$_2$O$_3$-nNiO calcined at

800°C. No desorption was observed for each support materials except for Al_2O_3. The single desorption peak from Pd was observed for Pd/Al_2O_3 and desorption over 700°C are ascribed from Al_2O_3. Another desorption peak, however, appeared around 750°C in addition to the desorption at low temperature for Pd/Al_2O_3-2NiO and Pd/Al_2O_3-36NiO. On the other hand, only a single desorption peak was observed for Pd/NiO. The total amount of oxygen desorption agreed with that expected from the conversion of PdO into Pd for every sample.

The crystalline phase of the support significantly affected the Pd3d spectra in Pd/mAl_2O_3-nNiO system. This interaction is also expected to affect the adsorbed oxygen species. Therefore, samples at the fixed composition of Pd/Al_2O_3-2NiO with different crystalline phases in the support were prepared. Preparation procedures of the supports are as follows. (a) Coprecipitation method, where ammonia solution was added to the mixed aqueous solution of nitrate until pH reached 7. (b) The method described in the Experimental section. (c) Mechanical mixing. Al_2O_3 and NiO were prepared by decomposition of aluminum and nickel nitrate at 800°C and the two oxide sup-

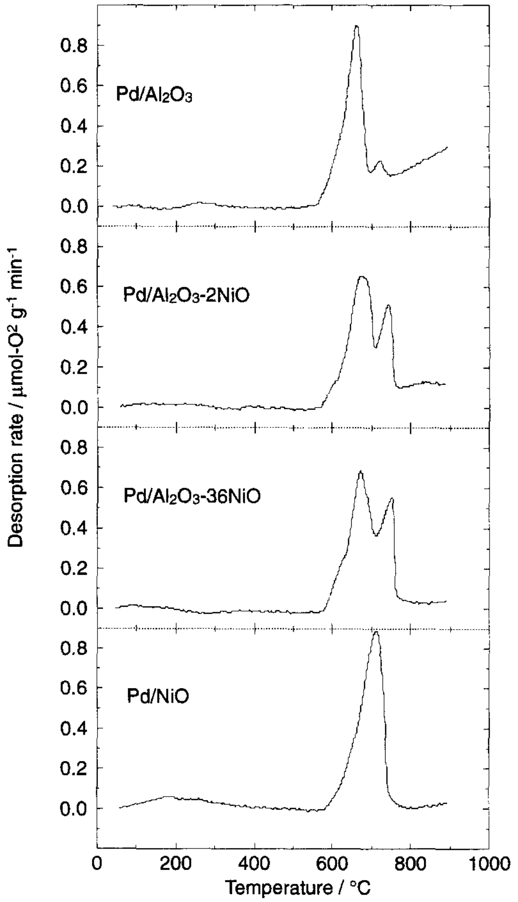

Fig. 5. TPD profiles of oxygen from 1.1 wt% Pd/mAl_2O_3-nNiO. Heating rate, 5°C min^{-1}.

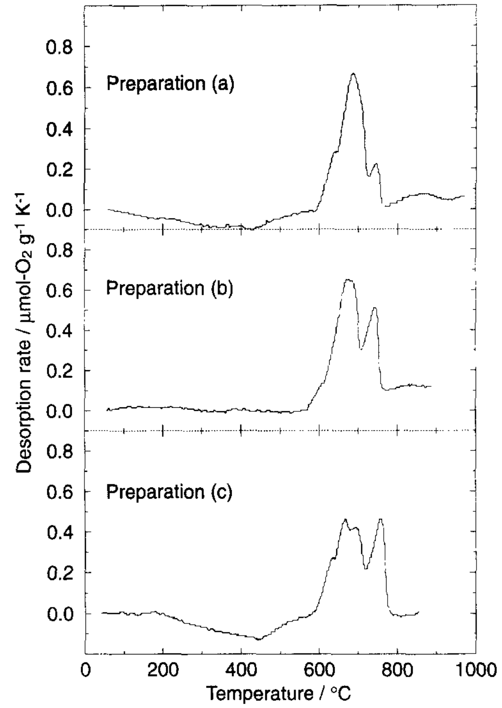

Fig. 6. TPD profiles of oxygen from 1.1 wt% Pd/Al_2O_3-2NiO with different crystalline phases. Heating rate, 5°C min^{-1}.

Table 2
Phases, surface areas, and catalytic activities of 1.1 wt% Pd/Al_2O_3-2NiO with different crystalline phases

	Surface area [a] (m^2 g^{-1})	Catalytic activity [b] T10/T30	Crystal phase of support [a]
a	61.8	365/420	$NiAl_2O_4$, small NiO
b	63.9	320/375	$NiAl_2O_4$, NiO
c	44.6	325/365	NiO

[a] Calcined at 800°C for 5 h.

[b] Temperatures at which methane conversions are 10 and 30%, respectively.

ports were ground together for sample (c). The TPD profiles of oxygen from these samples are shown in Fig. 6 and their catalytic activity, surface area, and crystal size of PdO are listed in Table 2. Catalytic activity of sample (a) was lower in spite of higher dispersion of palladium than sample (b). This low activity apparently results from deactivation by the $NiAl_2O_4$ support. The shape of desorption peak, which is different from that of other Pd/Al_2O_3-2NiO catalysts, implies that the interaction between palladium and oxygen depends on the support. Sample (b) and (c) gave a good result for the combustion of methane in spite of its low surface area in Pd/Al_2O_3-2NiO. These results indicate that a large amount of the NiO phase leads to high catalytic activity. It is revealed that Pd/mAl_2O_3-nNiO catalysts possess excellent catalytic activity as an ignition catalyst and that palladium can be deposited on low surface area support with a high dispersion.

4. Conclusions

Pd catalysts supported on Al_2O_3-based mixed oxides were investigated for catalytic combustion. Pd/mAl_2O_3-nNiO catalysts showed excellent catalytic activity. Particle size of palladium and crystal phase of support are the keys for enhancing the catalytic activity. The core level binding energy of palladium ($Pd3d_{5/2}$) is affected by the support and the crystal size. The increase in $NiAl_2O_4$ phase in the support deteriorates the catalytic activity in a series of Pd/mAl_2O_3-nNiO. Pd/Al_2O_3-36NiO demonstrated excellent activity for catalytic combustion at low temperatures.

Acknowledgements

Present work was partially supported by the Grand-in-Aid for Priority Areas from the Ministry of Education Science and Culture, Japan.

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