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Effects of Additives on the Activity of Palladium Catalysts for Methane Combustion

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Effects of metal oxide additions on the activity of Pd catalysts for CH_4 combustion were examined in this study. Since a high concentration of oxygen on Pd surface can be attained, the addition of metal oxide is useful for enhancing the oxidation activity of Pd. In particular, NiO added Pd catalysts are highly active for CH_4 combustion, and complete oxidation of CH_4 can be attained below 823 K.

Catalytic combustion, a new combustion technique without flames, is expected to be applicable to gas turbines.1) The advantages of oxidation catalysts for the application to combustion are the controllable combustion of various fuels, less emission of pollutants, and high efficiency of energy recovery. Barium hexaaluminate, $BaAl_{12}O_{19}$, is reported to exhibit high heat resistance,2,3) and oxidation catalysis can be sustained over 10000 h at 1673 K by the substitution of $BaAl_{12}O_{19}$ with cations such as Mn or Fe. However, oxidation activity of the Mn substituted $BaAl_{12}O_{19}$ is not high in a low temperature region, and consequently, precombustion of fuels with flames is required to heat the feed gas. However, nitrogen oxide (NO_x) is formed in this "precombustion region", which is the main origin of NO_x formation in catalytic combustors.4) Therefore, combustion catalysts with high oxidation activity is highly sought for the development of catalytic combustors with no NO_x emissions. In this study, we investigated the effects of additives on the oxidation activity of Pd for the improvement of oxidation activity in the low temperature region.

Alumina-supported binary Pd catalysts were prepared by the impregnation of an aqueous solution of $PdCl_2$ and metal nitrates. Alumina (Aerosil) with a BET surface area of 120 m^2/g was used as the support, and unless otherwise noted, the molar ratio of Pd to additives which were assumed to be the metallic state, was 9 and the total metal loading was 1.0 wt%. The obtained catalysts were reduced at 773 K for 4 h in a hydrogen stream and followed by calcination at 1073 K for 4 h in air. Oxidation activities were measured by the combustion of methane in a conventional flow system under atmospheric pressure. Catalysts were fixed in a quartz reactor after dilution with quartz beads. A gaseous mixture of methane (1 vol.%) and dry air (99 vol.%) was fed to the catalyst beds at a space velocity of 10^5 h^{-1}, which corresponds to a value in a practical gas turbine.

Table 1 summarizes the CH_4 combustion activity of the binary Pd catalysts examined in this study. In Table 1, the combustion activity is expressed as temperatures, T_{30}, T_{50}, T_{90}, and T_{100} at which CH_4 conversion levels of 30, 50, 90, and 100%, respectively. The dispersion of Pd strongly affected the combustion activity. However, XRD analysis suggested that the loaded Pd was highly dispersed on each catalysts and the difference in the dispersion of Pd between the catalysts was small. Consequently, the effects of Pd dispersion on the combustion activity should be negligible in this study. Since the temperature at each CH_4 conversion level becomes lower on most of the binary Pd catalysts comparing with pure Pd catalysts, addition of small amounts of metal oxides enhanced the activity of Pd to CH_4 oxidation. In particular, addition of NiO, SnO_2, or Ag_2O is effective for enhancing the oxidation activity of Pd catalysts.

Temperatures at 90% CH_4 conversion level (T_{90}) over the binary Pd catalysts were plotted versus the enthalpies of the reduction of added metal oxide in Fig. 1. Enthalpy (ΔH_{red}) of the reduction of additives in Fig. 1 is calculated by assuming that the additives are reduced from the oxidation states estimated by XRD analysis to the next stable reduced states. The temperature at T_{90} decrease as the values of ΔH_{red} increase and attain a minimum at NiO. It seems likely that a volcano-like rela-

Table 1. CH_4 combustion activity on the binary Pd catalysts on Al_2O_3

Catalysts	CH_4 combustion activity/K[a]			
	T_{30}	T_{50}	T_{90}	T_{100}
Pd	736	806	957	1003
Pd-NiO	623	653	748	813
Pd-SnO_2	648	703	783	853
Pd-Ag_2O	653	683	798	903
Pd-RhO	603	688	813	1003
Pd-Mn_3O_4	698	723	813	973
Pd-PtO	648	698	823	1003
Pd-PbO	663	733	833	1003
Pd-CoO	663	708	833	913
Pd-Fe_2O_3	673	733	853	973
Pd-Cr_2O_3	693	718	868	903
Pd-CeO_2	658	703	873	973
Pd-CuO	618	738	888	983

a) Temperature at the CH_4 conversion level of 30, 50, 90, and 100%.

tionship exists between the temperature T_{90} and ΔH_{red}, albeit slight deviations in some metal oxides are observed. This volcano-like relationship suggests that metal oxides added to Pd adsorb gaseous oxygen molecules, dissociates it to atomic oxygen, and then provides it to Pd. Consequently, a high level of oxygen concentration on the Pd surface can be attained by the additives, resulting in an elevation of oxidation activity. The improved oxygen concentration on Pd by the NiO addition was also reported by Hayata et al.$^{5)}$

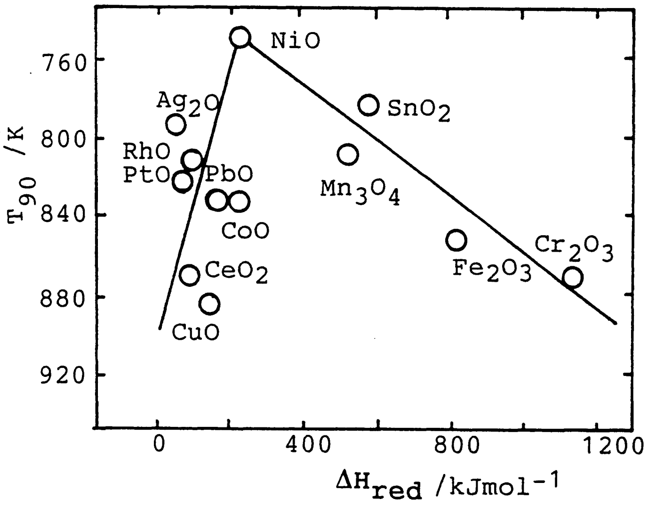

Fig. 1. Relationship between the temperature of T_{90} and ΔH_{red}.

Figure 2 shows the TG-DTA curves of Pd, and Pd added with NiO and SnO_2. A broad endothermic peak with weight loss was observed around 1200 K on all specimens, and this peak was attributed to the phase transition from PdO to Pd.$^{6)}$ It is apparent in Fig. 2 that the temperature at which phase transition occurs was shifted to a higher temperature by additions of NiO and SnO_2. This shift in phase transition to a higher temperature results from the improved oxygen concentration on Pd surface by the addition of NiO or SnO_2. As a result, metal oxides added to Pd behave as oxygen sources by the redox, and the high level of oxygen concentration on Pd surface can be sustained. In particular, addition of NiO or SnO_2 is effective for enhancing the oxidation activity of Pd because both the reduction and oxidation of NiO or SnO_2 proceeds easily.

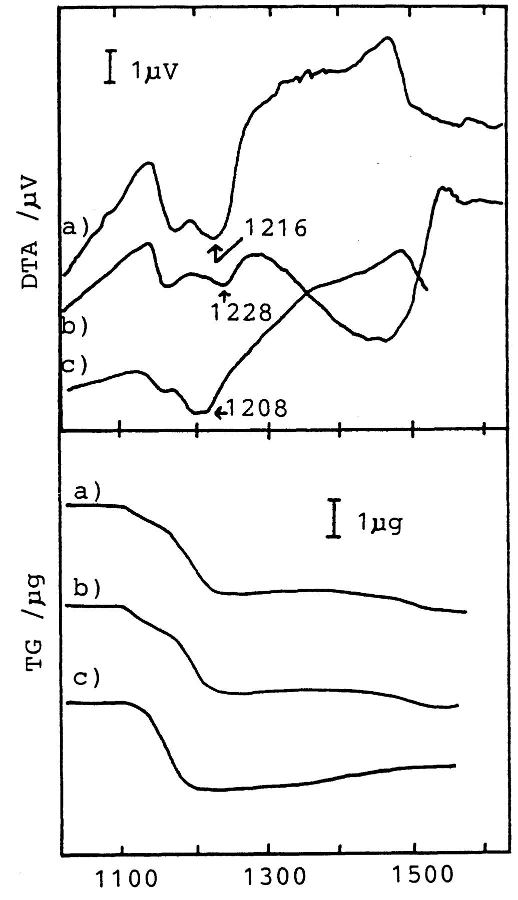

Fig. 2. TG-DTA curves of Pd, and Pd added with NiO and SnO_2. (Heating rate; 10 K/min) a)Pd-NiO, b)Pb-SnO_2, c) Pd.

The temperatures, T_{90} and T_{50}, on NiO added Pd catalysts were shown in Fig. 3 as a function of NiO content. The temperatures of T_{90} as well as T_{50} were decreased with increasing Ni content and attained a minimum when 10 mol% NiO was added to Pd. However, excess amount of Ni addition increased the temperature of T_{90} and T_{50}, because the activity of NiO to CH_4 combustion is extremely low. Therefore, the optimum amount of NiO addition was confirmed to be 10 mol%. The temperature dependence of CH_4 conversion on pure Pd and Pd catalysts added with 10 mol% NiO are shown in Fig. 4. CH_4 conversion on Pd/Al_2O_3 dipped with an increases in reaction temperature around 973 K and then attained 100 % conversion at 973 K. This activity decrease around 973 K is reported to be due to the dissociation of PdO to Pd metal.[6)] The dissociation of PdO to Pd occurred under CH_4 combustion in a lower temperature region as compared with the results in TG-DTA. This is because the temperature at the catalysts surface becomes higher than the average temperature of the catalyst bed. High CH_4 conversion was exhibited from low temperature regions on NiO added Pd catalysts, and moreover, a dip in the activity to the CH_4 combustion resulting from the phase transitions did not appear. As a result, complete oxidation of CH_4 can be attained by addition of NiO below 823 K which is ca. 200 K lower than that of pure Pd catalysts.

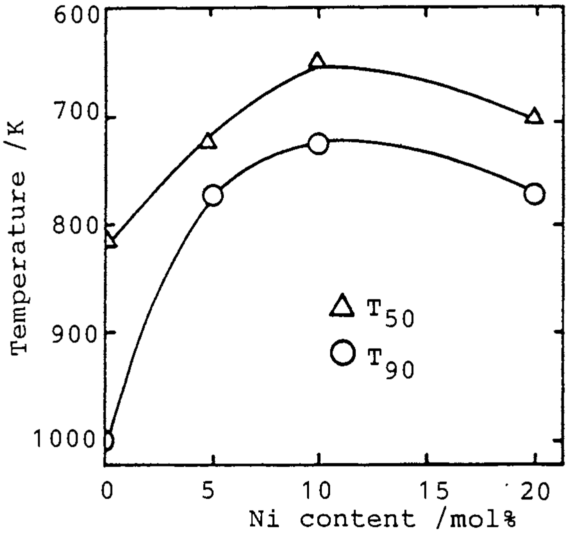

Fig. 3. The temperatures of T_{90} and T_{50} on Pd-NiO/Al_2O_3 as a function of Ni content.

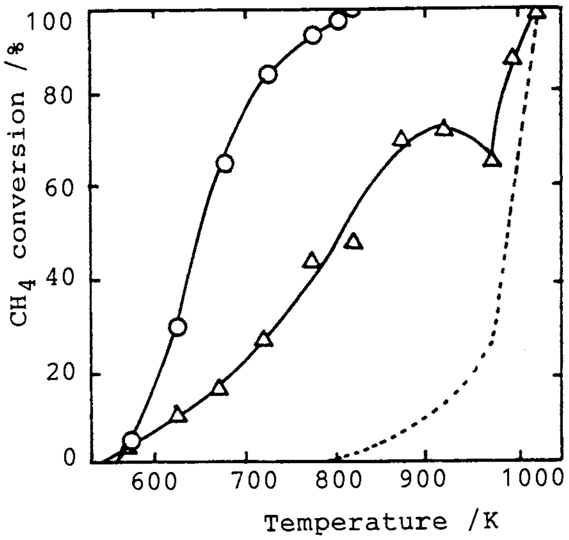

Fig. 4. Temperature dependencies of CH_4 conversion.
○ Pd-NiO △ Pd ····· Al_2O_3

References

1) Z.R. Ismagilov and M.A. Kerzhentsev, Catal. Rev. Sci. Eng., 32, 51 (1990).
2) M. Machida, K. Eguchi, and H. Arai, J. Catal., 103, 385 (1987).
3) M. Machida, K. Eguchi, and H. Arai, J. Catal., 123, 477 (1990).
4) H. Arai and M. Machida, Syokubai, 33, 328 (1991).
5) T. Hayata, T. Furuya, S. Yamanaka, and J. Koezuka, Shokubai, 31, 116 (1987).
6) G. Bayer and H.G. Wiedemann, Thermochim. Acta, 11, 79 (1975).

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