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Low temperature oxidation of methane over Pd catalyst supported on metal oxides

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Abstract

Supported Pd catalysts were investigated for low temperature oxidation of methane for catalytic combustor. Both, Pd/ZrO_2 and Pd/SnO_2 demonstrated excellent activity in spite of its low surface area. The activity of Pd/ZrO_2 was strongly dependent on the crystal phase of the support materials. ZrO_2 with a monoclinic phase enhanced the activity than that with a tetragonal phase. The catalytic activity of Pd/SnO_2 was affected by the preparation procedure. Impregnation of Pd on SnO_2 using $Pd(C_5H_7OO)_2$ aqueous solution was most effective in enhancing the catalytic activity. It is considered that catalytic activity is strongly influenced by the existence of interaction between palladium and support materials. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic combustion of natural gas is advantageous in increasing efficiency and in reducing emissions of air pollutants, such as CO, NO_x, and unburned hydrocarbons [1–3]. Some concepts have been proposed to attain ideal catalytic combustor for high temperature applications such as gas turbines [2,4]. For practical applications, two kinds of catalyst materials are required; one having high catalytic activity with a low ignition temperature, and the other possessing high heat resistance, catalytic activity, surface area, and thermal shock resistance. Some hexaaluminate compounds are the most promising catalysts as they are heat resistant materials with a fair catalytic activity. On the other hand, noble metal catalysts are the most active ignition catalysts, and supported palladium catalysts demonstrate the most excellent activity for oxidation of natural gas [5–7]. Although, many palladium catalysts have been investigated for their activity in the combustion of methane, more active materials are required for ideal complete catalytic combustion for gas turbines. Support materials play an important role in the field of heterogeneous catalysis, however, their performance is strictly related to the preparation procedure and to the nature of the support. In our previous studies, we have reported that Pd/Al_2O_3–36NiO and Pd/SnO_2 catalysts demonstrate excellent catalytic activity for low temperature oxidation of methane due to small particle size of palladium and metal–support interaction.

In this study, modification of supported palladium catalysts were investigated for low temperature ignition catalysts. In situ XRD and temperature-

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programmed-desorption (TPD) of oxygen were employed to evaluate the effect of the support. The relation between the catalytic activity and the physical and chemical properties of palladium particles supported on metal oxides were also discussed.

2. Experimental

2.1. Sample preparation

Commercial metal oxide powders MO_x (M=Al, In, Nb, Sn, Y, and Zr) were used as starting materials for oxide supports. These powders of oxides were calcined at 800°C for 5 h in air. Mixed oxide supports were prepared from aqueous solution of metal nitrates, chlorides, and sulfates with oxides. The resultant precursor was dried and calcined at 800°C for 5 h in air. Palladium catalysts were prepared by the impregnation method using a palladium nitrate solution and the oxide powders. The loading of palladium in its metallic state was 1 wt.% of the catalysts. The catalysts were dried and subsequently calcined in air at 800°C for 5 h. Specific surface area of catalysts was determined by the BET method using nitrogen adsorption.

2.2. Catalytic oxidation of methane

Catalytic combustion of methane over supported palladium catalysts was examined 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.%) and air (99 vol.%) was supplied at a space velocity of 48 000 h^{-1}. Methane conversion in the effluent gas was analyzed by on-line gas chromatograph.

2.3. Temperature-programmed-desoprtion (TPD) and -reoxidation (TPRO) measurement

The TPD of oxygen was carried out in a flow system to observe oxygen desorption from catalysts. A standard reaction vessel was used for the TPD experiment. A catalyst (1 g) was fixed in a quartz reactor by packing quartz wool at both ends. Prior to the measurement, the sample was reduced in a He flow (50 ml min^{-1}) at 800°C, followed by an O_2 flow (50 ml min^{-1}) at 800°C for 2 h. After cooling in O_2 to room temperature, the feed gas was switched to a He stream (50 ml min^{-1}) for TPD. The sample was heated at a rate of 5°C min^{-1} from room temperature to 800°C. After the TPD measurement and subsequent evacuation at 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 TPRO. The oxygen in the effluent gas was detected by using a TCD cell and a mass spectrometer (ULVAC, MSQ-150A).

3. Results and discussion

3.1. Catalytic oxidation of methane over Pd catalysts supported on single oxides

Catalytic activities for methane combustion over Pd catalysts supported on various oxides (MO_x; M=Al, Ga, In, Nb, Sn, Si, Ti, Y, and Zr) are summarized in Table 1. The overall activity of the catalyst was characterized by temperatures at which methane conversion reaches 10, 30, 70, and 90%, as expressed by T_{10}, T_{30}, T_{70}, and T_{90}, respectively. In every case, no reaction products except carbon dioxide and water were detected. The oxidation of methane over Pd/Al_2O_3 started at about 300°C followed by a steep increase in conversion up to 100% at 800°C. The

Table 1
Methane oxidation over Pd catalysts supported on various oxides

Catalyst	Surface area[a] (m^2 g^{-1})	Catalytic activity[b]			
		T_{10}	T_{30}	T_{70}	T_{90}
Pd/Al_2O_3	109.1	365	400	445	495
Pd/Ga_2O_3	–	365	420	765	815
Pd/ln_2O_3	5.1	390	440	520	590
Pd/Nb_2O_5	–	565	665	840	875
Pd/SiO_2	108.3	420	585	680	860
Pd/SnO_2	6.4	325	355	390	440
Pd/TiO_2	–	400	720	840	885
Pd/Y_2O_3	–	505	565	635	700
Pd/ZrO_2	5.6	325	355	400	490

[a] Calcined at 800°C.

[b] Temperature at which methane conversion is 10, 30, 70, and 90%, respectively. Reaction conditions: CH_4, 1 vol.%; air, 99 vol.%; space velocity, 48 000 h^{-1}.

catalytic activity increased monotonically with increasing temperature. Surface areas of the catalysts on other metal oxide supports were extremely low as compared with that of Pd/Al_2O_3 except Pd/SiO_2. However, Pd/ZrO_2 and Pd/SnO_2 catalysts demonstrated higher activity than that of Pd/Al_2O_3 at all reaction regions and the sequence of the catalytic activities was M=Sn>Zr>Al>Ga>In>Ti>Si>Y>Nb. These results indicate that no simple correlation could be found between the activity and the BET surface area. Complete combustion over Pd/ZrO_2 and Pd/SnO_2 could be achieved at lower temperatures than over Pd/Al_2O_3. Therefore, supported palladium catalysts with mixed oxides based on ZrO_2 and/or SnO_2 were prepared and investigated.

3.2. Catalytic oxidation of methane over Pd/ZrO_2–MO_x (M=Co, Cr, Cu, Fe, Mn, and Ni)

Catalytic activities and surface areas of Pd supported on various ZrO_2-based mixed oxides (Pd/ZrO_2–MO_x; M=Co, Cr, Cu, Fe, Mn, and Ni) are summarized in Fig. 1. Surface areas and catalytic activities were different depending on the additive species M. The surface area of Pd/ZrO_2 (11.6 $m^2\,g^{-1}$) was lowered with the addition of transition metals except for Cr. The catalytic activity was significantly retarded by the presence of metal oxides incorporated in the ZrO_2 support. The sequence of the catalytic activities below 500°C was M=Zr>Co=Ni>Fe=Mn=Cr>Cu. No simple correlation could be found between the catalytic activity and the BET surface area in this series of catalysts.

Crystal phase of the support material sometimes gives different physical and/or chemical properties for the active species. Generally, a ZrO_2 support exists in monoclinic and tetragonal crystalline forms. Monoclinic zirconia is thermodynamically stable below 1150°C [8], whereas tetragonal zirconia, formed at higher temperatures can exist as a metastable phase at lower temperatures [9–11]. To reveal the influence of crystalline phase of the ZrO_2 support on the activity, the Pd/ZrO_2 catalyst with different crystalline phases in the ZrO_2 support were prepared. The supports were prepared as follows: (a) commercial powder of ZrO_2; (b) thermal decomposition of aqueous solution of $ZrO(NO_3)_2$; (c) thermal decomposition of aqueous solution of $ZrO(NO_3)_2$ with 1 N H_2SO_4. All the samples were calcined at 800°C for 5 h prior to introducing Pd. The X-ray diffraction patterns of the Pd/ZrO_2 catalysts are presented in Fig. 2. The XRD pattern of sample (a) indicated the presence of only monoclinic crystalline zirconia, while the others showed the formation of the tetragonal phase of ZrO_2. The results of methane combustion experiments and BET surface area of these Pd/ZrO_2 catalysts are summarized in Table 2. It is apparent that the sample (a) has the highest activity among the others, whereas the BET surface area of the samples are almost the same. It is

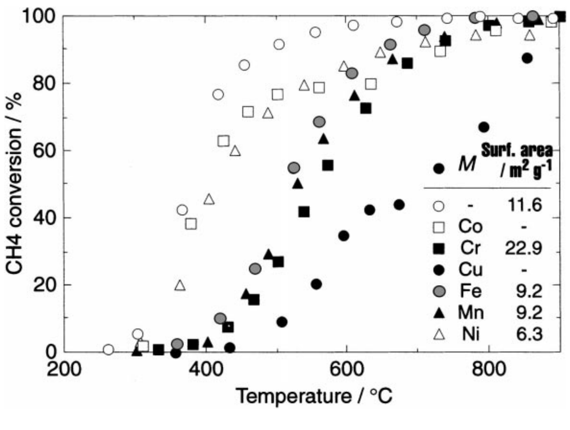

Fig. 1. Catalytic combustion of methane over 1 wt.% Pd/ZrO–Mo_x (M=Co, Cr, Cu, Fe, Mn, and Ni). Reaction conditions: CH_4, 1 vol.%; air, 99 vol.%; space velocity, 48 000 h^{-1}.

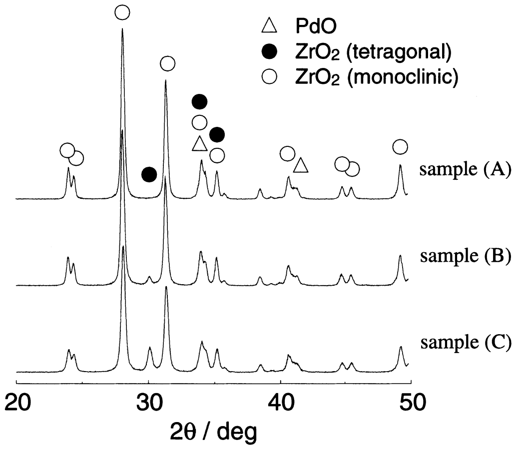

Fig. 2. X-ray diffraction patterns of 1 wt.% Pd/ZrO_2 with different preparation procedure.

Table 2
Phases, surface areas, and catalytic activities of 1 wt.% Pd/ZrO_2 with different crystalline phases

	Surface area[a] ($m^2\,g^{-1}$)	Catalytic activity[b]				Crystal phase of support[c]
		T_{10}	T_{30}	T_{70}	T_{90}	
(a)	11.6	320	350	400	450	m
(b)	11.5	320	350	410	485	m, t
(c)	15.3	320	350	435	515	m, t

[a] Calcined at 800°C.

[b] Temperature at which methane conversion is 10, 30, 70, and 90%, respectively. Reaction conditions: CH_4, 1 vol.%; air, 99 vol.%; space velocity, 48 000 h^{-1}.

[c] m, monoclinic; t, tetragonal.

noted that the increase in the amount of the tetragonal phase leads to lower the activity as seen in sample (c).

The effects of ZrO_2 support were reported in other investigations. Narui et al. [12] observed the interaction between PdO and ZrO_2, like solid solution. Müller et al. [13] reported that turnover frequency (TOF) of palladium was influenced by the dispersion of Pd on the ZrO_2. It is important that not only the quality of the active species such as TOF but also the quantity (number of active sites) is deeply related to the catalytic activity. Although, monoclinic ZrO_2 with high specific surface area is desirable to the catalytic activity, the ZrO_2 support generally possesses quite low surface area. Therefore, SiO_2 was employed to disperse the active species. $m$$ZrO_2$–$n$$SiO_2$ was prepared by impregnating silicic acid powder with a solution of $ZrO(NO_3)_2$ at an appropriate ratio. Fig. 3 shows the catalytic activity and BET surface area. The surface area of Pd/$m$$ZrO_2$–$n$$SiO_2$ increased with increasing SiO_2 content. However, the maximum activity was achieved at the composition of Pd/ZrO_2–SiO_2. XRD patterns of these catalysts are shown in Fig. 4. Monoclinic zirconia is the dominant phase over Pd/ZrO_2 and tetragonal zirconia is observed as a minor product. However the monoclinic phase rapidly decreased with increasing SiO_2, and only the tetragonal phase was remaining at Pd/ZrO_2–8SiO_2. From these results, it can be inferred that the crystalline phase of zirconia depends on the additive. The crystalline phase appears to affect the catalytic activity in addition to the enlargement of surface area by mixing with SiO_2. The composition of Pd/ZrO_2–SiO_2 (Zr/Si=1) is considered to be best for high catalytic activity.

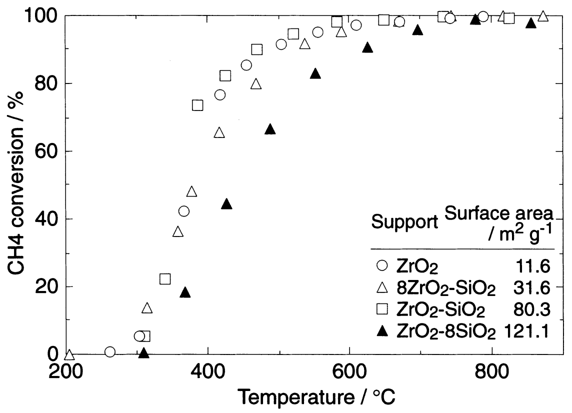

Fig. 3. Catalytic combustion of methane over 1 wt.% Pd/$m$$ZrO_2$–$n$$SiO_2$. Reaction conditions: CH_4, 1 vol.%; air, 99 vol.%; space velocity, 48 000 h^{-1}.

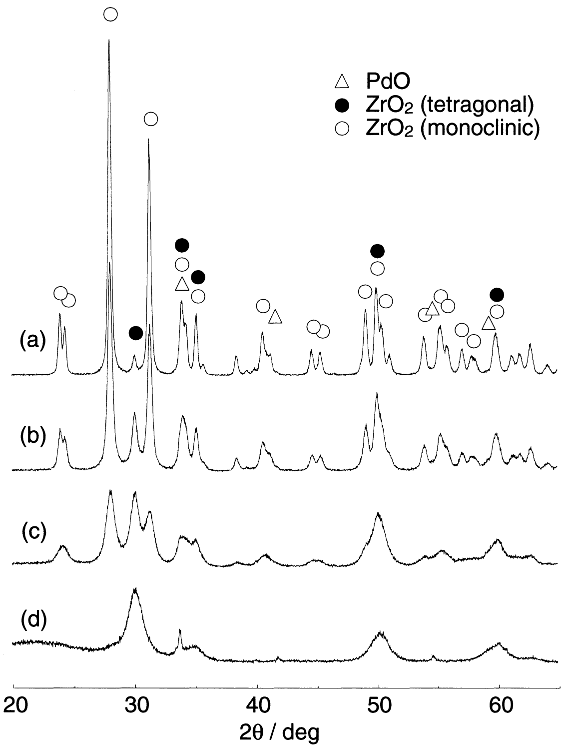

Fig. 4. X-ray diffraction patterns of 1 wt.% Pd/$m$$ZrO_2$–$n$$SiO_2$ calcined at 800°C for 5 h: (a) Pd/ZrO_2; (b) Pd/SiO_2–8ZrO_2; (c) Pd/SiO_2–ZrO_2; and (d) Pd/8SiO_2–ZrO_2.

To evaluate the correlations between the catalytic activity and the reduction–oxidation properties of supported Pd, TPD of oxygen and TPRO experiments were performed. Fig. 5 shows the TPD profiles of

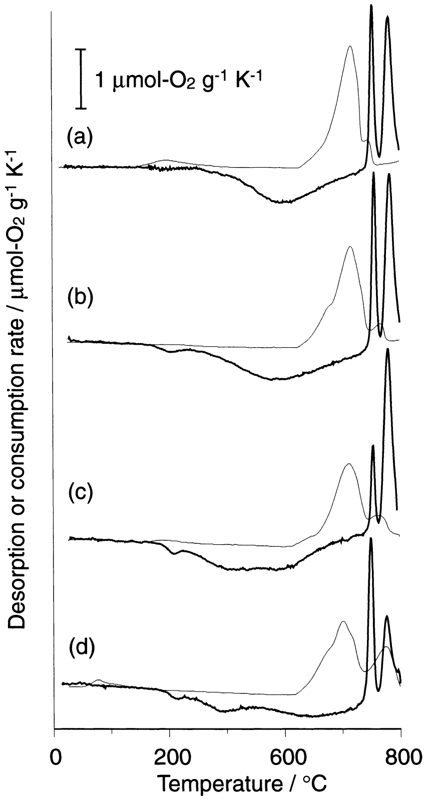

Fig. 5. TPD (thin line) and TPRO (thick line) profiles of oxygen from (a) Pd/ZrO_2; (b) Pd/8ZrO_2–SiO_2; (c) Pd/ZrO_2–SiO_2; and (d) Pd/ZrO_2–8SiO_2. Heating rate, 5°C min^{-1}.

oxygen from Pd/*m*ZrO_2–*n*SiO_2. In Pd/*m*ZrO_2–*n*SiO_2, some distinct peaks were observed at ca. 660 and 720°C. These peaks reflect the different adsorption state of oxygen on palladium. The peak temperature at about 660°C agreed with the thermodynamic dissociation of bulk PdO and the other is assigned to stable oxide species (PdO_x) [14–16]. The sequence of intensities of these desorption peaks were changed and shifted to the high temperature side with decreasing Zr content in the support. After TPD measurement, the sample was heated in the presence of oxygen to record as TPRO profiles. For every sample, reoxidation took place above 200°C, and the oxygen was desorbed from the catalyst above 720°C as well as in the TPD measurements, and two distinct peaks were observed at ca. 750 and 780°C. Since the O_2 uptake below 720°C is nearly equal to O_2 desorption above 720°C, a reversible reoxidation of metallic Pd phases proceeds in the TPRO process. The peak observed at about 750°C can be attributed to the bulk palladium and the other is assigned to PdO_x. It is inferred that the second peak is attributable to the desorption from Pd under strong support interaction. This second peak (780°C) is the maximum at the composition of Pd/ZrO_2–SiO_2, and it can be considered that the support effects are very important in determining catalytic activity. Further investigation is still necessary for revealing the relationship between adsorbed oxygen and catalytic activity.

The use of zirconia as a support for palladium is beneficial for combustion reactions and is very important in determining catalytic activity which can be modified by considering the preparation method for monoclinic zirconia.

3.3. Catalytic oxidation of methane over Pd/SnO_2

Pd/SnO_2 was found to have an excellent activity for the complete oxidation of methane, though the BET surface area of the SnO_2 support was far smaller than that of Al_2O_3. Our previous study has revealed that the PdO phase was well-dispersed on the outer surface of small SnO_2 particles, and that the PdO phase was stabilized at higher temperatures than bulk PdO without support materials. The catalytic activity is strongly influenced by the interaction between palladium and SnO_2. Therefore, it is desirable to enhance the catalytic activity by different preparation procedures of Pd/SnO_2 such

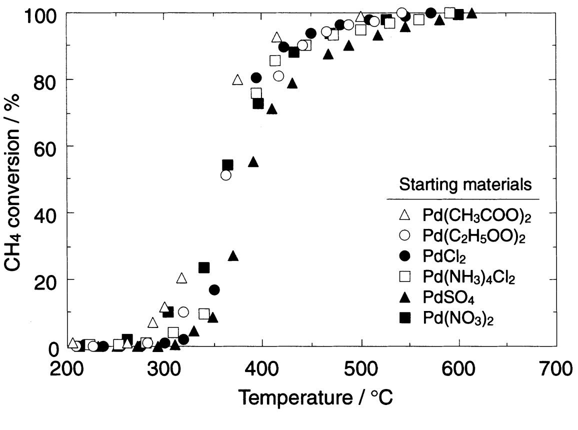

Fig. 6. Catalytic combustion of methane over 1 wt.% Pd/SnO_2. Reaction conditions: CH_4, 1 vol.%; air, 99 vol.%; space velocity, 48 000 h^{-1}.

as, the starting materials and heat treatment. Fig. 6 summarizes the catalytic oxidation of methane over Pd/SnO_2 with different starting materials of palladium. Pd/SnO_2 catalysts were prepared by an impregnation method using $Pd(CH_3COO)_2$, $Pd(C_5H_7OO)_2$, $PdCl_2$, $Pd(NH_3)_4Cl_2$, $Pd(NO_3)_2$, and $PdSO_4$ solution and the oxide powders. $Pd(CH_3COO)_2$ is the most suitable material for preparing of Pd/SnO_2, and the sequence of the catalytic activities at low temperatures was $Pd(CH_3COO)_2>Pd(C_5H_7OO)_2>Pd(NO_3)_2>Pd(NH_3)_4Cl_2>PdCl_2>PdSO_4$. Pd salts including Cl or S are not suitable materials, since these salts were left on the catalyst after calcination (800°C), and inhibited the catalytic reaction. Narui et al. [17] studied the effect of the palladium salts for preparation of Pd/Al_2O_3. They found that the catalytic activity decreased in the order of $Pd(C_5H_7OO)_2>Pd(CH_3COO)_2>Pd(NO_3)_2$. This corresponds to the sequence of the average particle size of palladium. Although it is difficult to estimate the dispersion of palladium in the egg-shell shaped structure of Pd/SnO_2, it is required to optimize the starting materials and heating process to prepare Pd/SnO_2 by taking the operating conditions into consideration.

4. Conclusions

Supported Pd catalysts were investigated for low temperature oxidation of methane for catalytic combustor. Pd/ZrO_2–SiO_2 and Pd/SnO_2 demonstrated excellent catalytic activities. The oxidation reaction over Pd/ZrO_2 affected the crystal phase of ZrO_2. The palladium supported on monoclinic ZrO_2 was higher than that on tetragonal ZrO_2. The catalytic activity of Pd/SnO_2 was affected by the preparation procedure. These results indicate that optimization of the starting materials and heating process to prepare Pd/SnO_2 is effective for enhancing the catalytic activity. To enhance the catalytic activity, it is required to improve the activity of the reaction center through Pd–support interaction and high dispersion of the active sites.

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