Catalytic Combustion of Methane over Pd Supported on Metal Oxides

Hardiyanto Widjaja, Koshi Sekizawa, and Koichi Eguchi*
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga, Fukuoka 816

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A Pd/SnO_2 catalyst demonstrated excellent activity for low temperature catalytic combustion of methane inspite of its low surface area. Palladium clusters were observed as an intimately contacted layer on fine SnO_2 particles. Temperature programmed desorption of oxygen revealed that methane combustion was found to be dependent on the adsorption state of oxygen on palladium. It is considered that catalytic activity is strongly influenced by the existence of interaction between palladium and tin oxide.

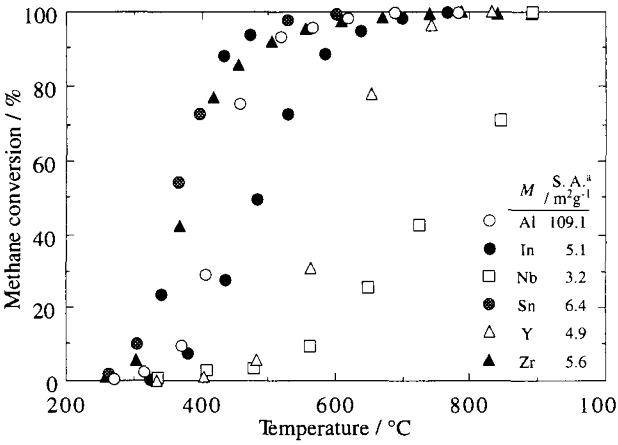
Catalytic combustion of methane, which is a main component of natural gas, has attracted attention of a large number of researchers because of its significance in eliminating or greatly reducing the amount of NO_X.[1,2] The initiation of the combustion at sufficiently necessary low temperatures can be achieved only by use of highly active catalysts. Nowadays, a highly active material is greatly requested as an ignition catalyst for the inlet zone combustor of gas turbines and other systems with heat extraction application operated over 1000 °C.[3]

Palladium has been known as the most active material for the combustion of methane.[4] Pd/Al_2O_3 is widely used as a catalyst for this application due to its high specific surface area and low cost.[5,6] Since the activity of the Pd/Al_2O_3 catalyst is insufficient below 350 °C, a catalyst with higher activity to make ignition temperature lower is still greatly requested.

In this study, catalytic activities of palladium supported on various metal oxides were investigated for designing active ignition catalyst for methane combustion. Transmission electron microscopy (TEM) observation and temperature-programmed desorption (TPD) of oxygen were employed to evaluate the morphology of palladium particles on the support and the effect of the support on the reduction-oxidation properties of Pd species, respectively.

Support oxides, MO_X (M = Al, In, Nb, Sn, Y, and Zr) were obtained from commercial metal oxide powders. These powders of oxides were calcined at 800 °C in air. Palladium catalysts were prepared by an impregnation method using a palladium nitrate solution and the oxide powders. The loading of palladium in its metallic state was 1.0 wt% of the catalysts. The catalysts were dried and subsequently calcined in air at 800 °C. Activities of the catalysts for the combustion of methane were determined in a conventional flow reactor operating at atmospheric pressure. The catalyst was fixed in a quartz reactor by packing alumina beads at both ends of the catalyst. Temperature-programmed-desorption (TPD) of oxygen was employed in a flow system to observe oxygen desorption from catalysts. Prior to the measurement, the sample was exposed in He flow at 800 °C, followed by O_2 flush at 800 °C. After cooling in O_2 to room temperature, the feed gas was switched to a He stream. TPD was performed at a heating rate of 5 °C min^{-1} up to 800°C.

Catalytic activities for methane combustion over Pd catalysts supported on various oxides, MO_X (M = Al, In, Nb, Sn, Y, and Zr) are summarized in Figure 1. In the case of Pd/Al_2O_3, the reaction started at about 300 °C followed by the steep increase in conversion up to 100% at 800 °C. The catalytic activity increased monotonously with rising temperature. Surface area of the catalysts on other metal oxide support were very low as compared with that of Pd/Al_2O_3. However, Pd/ZrO_2 and Pd/SnO_2 catalysts exhibited higher activity than Pd/Al_2O_3 at all reaction temperatures. The activity of Pd/ZrO_2 and Pd/SnO_2 at this condition increased gradually with time-on-stream before attaining the steady state. The steady state activities of Pd/ZrO_2 and Pd/SnO_2 were higher than that of Pd/Al_2O_3. The sequence of the catalytic activities was M = Sn > Zr > Al > In > Y > Nb. No simple correlation could be found between the catalytic activity and the surface area. Generally, the large support surface is often necessary for attaining high dispersion; however, for the present Pd catalysts, the catalytic activity may be influenced by dispersion state of Pd species and its oxidation state. The Pd/SnO_2 catalyst which was most active in Figure 1 was investigated in detail.



[a]BET surface area

Figure 1. Catalytic combustion of methane over Pd/MO_X (M = Al, In, Nb, Sn, Y, and Zr) catalysts. Reaction conditions : CH_4, 1vol%; air, 99vol%; space velocity, 48 000 h^{-1}.

High resolution TEM was employed for direct observation of Pd particles on SnO_2 (Figure 2). An Energy Dispersed X-ray analysis (EDX) indicated that each particle contained Sn and Pd. It is noted that shell and core structure could be obviously seen in the high resolution image. An amorphous-like Pd layer is forming the outer shell part of the particle, whereas the core region is well-crystallized SnO_2. Most of the particles equally possessed such a microstructure in this condition. This microstructure is obviously different from that of Pd/Al_2O_3 in which only fine dispersed grains of palladium are deposited on the support oxide. The Pd layer, uniformly covering the SnO_2 fine particles, leads to a high dispersion state of palladium by subsequent heating at higher temperatures. It can be inferred that the palladium layer on the SnO_2 support is transformed into fine palladium particles which are strongly interacting with the support.

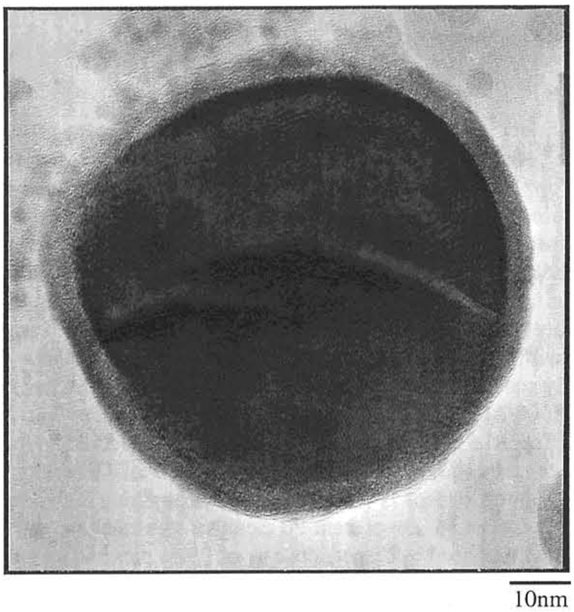


Figure 2. High resolution TEM image of 1.0wt%Pd/SnO_2.

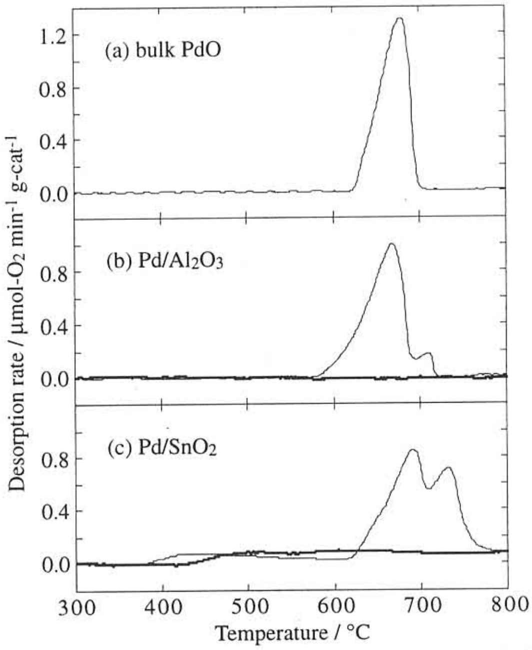


Figure 3. TPD profiles of oxygen from bulk PdO, Pd/Al_2O_3, and Pd/SnO_2. Heating rate = 5 °C min^{-1}. Sample was heated in O_2 stream at 800 °C for 2 h and followed by cooling to room temperature prior to the measurement.

——— bulk PdO or supported Pd
——— support only

To evaluate the correlations between the catalytic activity and the reduction-oxidation property of supported Pd, TPD experiments were then performed. Figure 3(a) shows the TPD profiles of oxygen from bulk palladium without support. It features a sharp oxygen release centered at *ca.* 680 °C. This desorption behavior is similar to that observed by Bell *et al.*,[7] and assigned to the oxygen desorption resulting from dissociation of the PdO bulk. The PdO phase becomes thermodynamically unstable around this temperature; thus, the peak accompanies the decomposition of the bulk oxide into metallic Pd.

The TPD curves of oxygen from the supported Pd catalysts (Pd/Al_2O_3 and Pd/SnO_2) are also shown in Figure 3(b) and 3(c). No desorption of oxygen was detected from the Al_2O_3 support, while the SnO_2 support exhibited a small and broad desorption of oxygen from 430 °C. It is revealed that the TPD profiles of oxygen from the two kind of supported palladium considerably differ from the single desorption peak from bulk palladium without the supports. For the supported Pd samples, oxygen desorption in the temperature range of 600-750 °C split into two peaks. For Pd/Al_2O_3, two distinct peaks were observed at *ca.* 660, and 720 °C. Therefore, these peaks reflect the different adsorption state of oxygen on palladium. The desorption curve of oxygen from the active Pd/SnO_2 was characterized by two oxygen species which desorb at higher temperatures than less active catalyst (Pd/Al_2O_3). Especially, the Pd/SnO_2 catalyst exhibited large desorption of the second peak. Thus, significant differences are observed in TPD curves of Pd on different supports. The broad peak observed at low temperatures from Pd/SnO_2 can be attributed to oxygen released from the SnO_2 support.

Comparison of the TPD profiles indicates that oxygen desorption between 660-680 °C is attributed to bulk PdO without the support interaction. The peak observed at about 720 °C can be attributed to stabilized oxide form of palladium (PdO_x).[8] Thus, it may be inferred that the second peak is attributable to the desorption from Pd under strong support interaction. It can be considered that the support effects observed as the second peak for Pd/SnO_2 is also very important in determining catalytic activity, since the high oxidation state of palladium has been known to be responsible for high combustion activity. Further investigation is still necessary for revealing the relationship between adsorbed oxygen and catalytic activity.

References and Notes

1 R. Prasad, L. A. Kennedy, and E. Ruckenstein, *Catal. Rev.-Sci. Eng.*, **26(1)**, 1 (1984).
2 D. L. Trimm, *Appl. Catal.*, **7**, 249 (1983).
3 H. Sadamori, T. Tanioka, and T. Matsuhisa, *Proc. 2nd Int. Work shop Catal. Combust.*, **1994**, 158.
4 R. F. Hicks, H. Qi, M. L. Young, and R. G. Lee, *J. Catal.*, **122**, 280 (1990).
5 C. F. Cullis and B. M. Willat, *J. Catal.*, **83**, 267 (1983).
6 J. G. E. Cohn and A. J. Haley, *Can. Pat.*, **597**, 459 (1960).
7 W. E. Bell, R. E. Inyard, and M. Tagami, *J. Phys. Chem.*, **70**, 3735 (1966).
8 J. G. McCarty, *Catal. Today*, **26**, 283 (1995).