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Development of a catalytic burner with Pd/NiO catalysts

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Abstract

A catalytic burner was studied which can be used as a heater operated at medium temperature. The catalytic combustion was initiated by an igniter which was placed on the exit surface of the catalyst layer. Noble metal catalysts (Pd/NiO) which were supported on alumina washcoated honeycomb were used, whose maximum heat-resisting temperature is about 900°C. The optimal operating conditions for stable catalytic combustion were obtained by means of analyzing the catalytic combustion region, the temperature distribution, and the combustion efficiency.

Keywords: Catalytic combustion; Pd/NiO catalyst; Honeycomb; Methane catalytic combustion

1. Introduction

Catalytic combustion is a phenomenon in which fuel and oxidant react on a catalyst surface. It was mostly used for small sized heaters in the early stage of the development. In recent years much research on catalytic combustion has been extensively focused on the development of low NO_x combustors [1–4].

Catalytic combustion has some special features as compared to ordinary flame combustion. Firstly, it has a lower lean limit of flammability than flame combustion. Even lean mixtures that cannot be burned by gas combustion can be burned by catalytic combustion. The adiabatic flame temperature decreases as a mixture becomes more lean. Therefore if catalytic combustion is applied to any combustion system, it is possible to keep its flame temperature low enough to prevent production of thermal NO_x [5,6].

Secondly, the light-off temperature of catalytic combustion is lower than the ignition temperature of gas combustion, because the activation energy for the catalytic surface reaction is much less than that for gas-phase reaction. For example, gas combustion has an ignition temperature of 615°C for methane, but catalytic combustion has a light-off temperature of below 400°C even though it depends on the kind of catalysts and reaction conditions employed. By using these merits of catalytic combustion, catalytic combustors for gas turbines with low NO_x have been actively studied [7,8].

Objective of this study is to develop an industrial catalytic burner of natural gas with noble metal catalysts (Pd/NiO). Although catalytic combustion systems for gas turbines have pre-heating equipment, industrial catalytic burners without pre-heating unit will be competitive to the existing burners using flame

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combustion. Therefore the goal of this study is the development of a catalytic heater without pre-heating unit providing the advantages of low NO_x emissions and high efficient radiation from catalytic combustion.

Experimental investigations of catalytic combustion of methane in the Pd/NiO catalyst-washcoated honeycomb monolith are presented.

2. Experimental

2.1. Apparatus

The schematic diagram of the experimental equipment is shown in Fig. 1. It consists of a fuel and an air supply system, a catalytic burner, a temperature measurement system, and an analysis system of the combustion gas. Fuel of methane (99.9%) was supplied at a proper flow rate through a governor and a mass flow controller. Compressed air was used and moisture and mist in air were removed by a series of filters.

The dimension of the catalytic burner was 10 cm long×10 cm wide×40 cm high. A honeycomb uniformer of 400 cells/in.^{2} was placed in the center of the burner to get a uniform flow in the catalyst layer. The catalytic burner was insulated with ceramic papers of 5 mm in thickness. The premixed gas was supplied from the bottom of the burner. It passes first through the honeycomb uniformer and then enters the catalyst layer. A thermocouple and a sampling probe were installed inside the catalyst layer to measure temperatures and to analyze combustion gas, respectively. An auto traverse unit was used to move them to the desired positions.

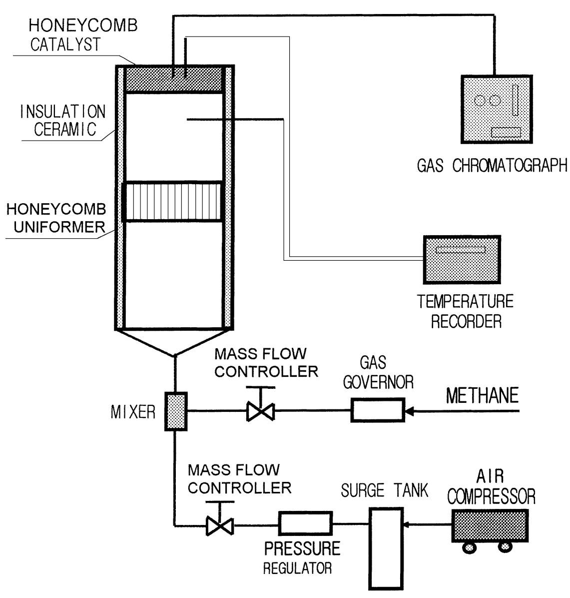

Fig. 1. Schematic diagram of the experimental equipment.

2.2. Catalyst preparation

The honeycomb (cordierite) of 400 cells/in.^{2} was washcoated by a stabilized alumina. The Pd/NiO catalysts were prepared by impregnation with aqueous nickel and palladium salts, drying and calcining at 800°C for 4 h. Its maximum heat-resisting temperature was about 900°C. The size of catalysts used here was a square of 89 mm×89 mm with 15, 30, and 60 mm in thickness, respectively.

2.3. Procedure

An igniter was installed at the top of the catalyst exit for initiating catalytic combustion. The catalyst layer was warmed up by the heat of the flame until catalytic combustion was initiated and stabilized. As catalytic combustion took place on the surface of the catalyst exit and then slowly moved into the whole catalyst layer, flame combustion of mixture gas disappeared gradually. There were no indications of the catalyst being damaged by the flame, since the flame temperature on the upper surface of the catalyst was less than 900°C.

To analyze the combustion gas the sample probe (0.7 mm OD, SS) was vertically inserted down to the center of the catalyst layer as controlled by the traverse unit. The sampling rate was 3 ml/min without interfering with the progress of the catalytic combustion. A gas chromatograph (model: Schimadzu GC-9A) with TCD was used for analyzing the combustion gas. The conversion of methane was obtained by means of analyzing the concentration of CH_4 and CO_2.

The temperature of the catalyst layer was measured by a K-type thermocouple (ϕ 0.1 mm). It was vertically inserted into the catalyst layer and controlled by the same way as the sample probe.

The temperature distribution in the catalyst layer was measured under various operation conditions to obtain the temperature characteristics of the catalytic burner.

3. Results and discussion

3.1. Temperature characteristics

Fig. 2 shows the temperature of the 30 mm thick catalyst layer at various excess air ratios. The temperature was measured from catalyst inlet to catalyst exit at the center line of the catalyst layer.

The temperature of the catalyst layer increased with the increase of excess air. It rose rapidly just from the entrance of the catalyst layer and decreased smoothly after passing through a maximum. The maximum temperature existed near the inlet of the catalyst layer indicating that the catalytic oxidation reaction was very fast.

The location of the maximum temperature moved slightly toward the catalyst exit as the excess air increased. The temperature of the catalyst inlet increased as the excess air ratio increased up to 1.25, but it decreased thereafter. This implies that the unpreheated mixture started to cool down the inlet side surface of the catalyst.

It is desirable for an industrial radiant burner to have the temperature of the catalyst exit as high as possible.

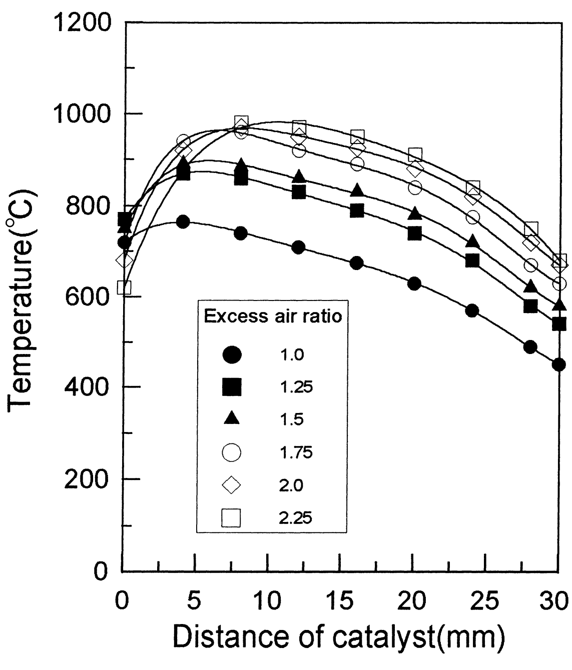

Fig. 2. Effects of the excess air on the temperature distribution of the catalyst layer.

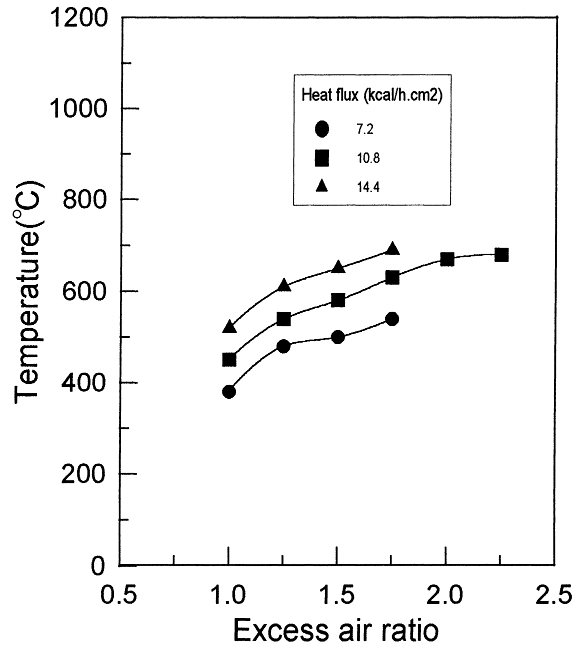

Fig. 3. Effects of the excess air and the heat flux on temperature of the exit of the catalyst layer.

Fig. 3 shows the temperature of the catalyst exit for the various excess air ratios and the various heat fluxes. The exit temperature of the catalyst layer rose with increasing excess air, because the position of the maximum temperature moved toward the downstream with the excess air as described before. It also rose as the heat flux increased, since the maximum temperature increased with heat flux.

Fig. 4 represents the temperature distribution of the catalyst layer with various heat fluxes. The temperature of the catalyst layer increased almost linearly with the heat flux. The location of the maximum temperature remained at almost the same position regardless of variation of the heat flux.

When the catalytic combustion was initiated with an igniter, the pattern of catalytic combustion was sensitive to operation conditions. Fig. 5 shows the results of the patterns of catalytic combustion and their temperature distribution. The catalytic combustion of a mixture occurred within the catalyst layer with an excess air ratio 1.0–1.5, whereas it did not occur with an excess air ratio 1.75–2.0. In the latter case the flame was observed on the surface of the

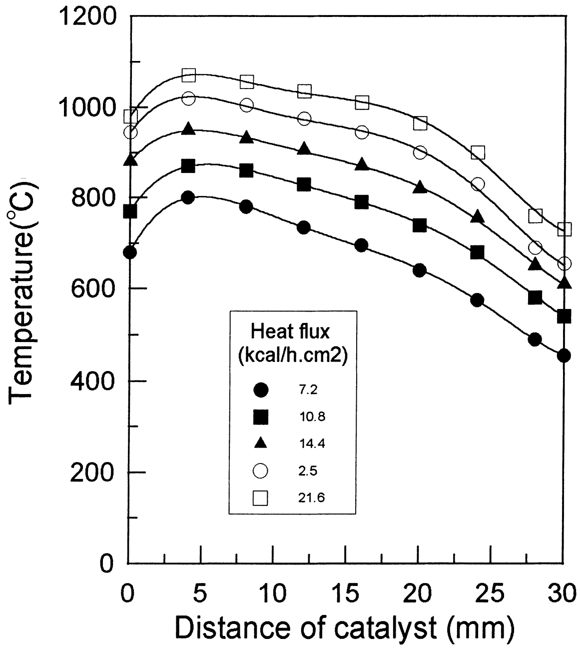

Fig. 4. Effects of the heat flux on the temperature distribution of the catalyst layer.

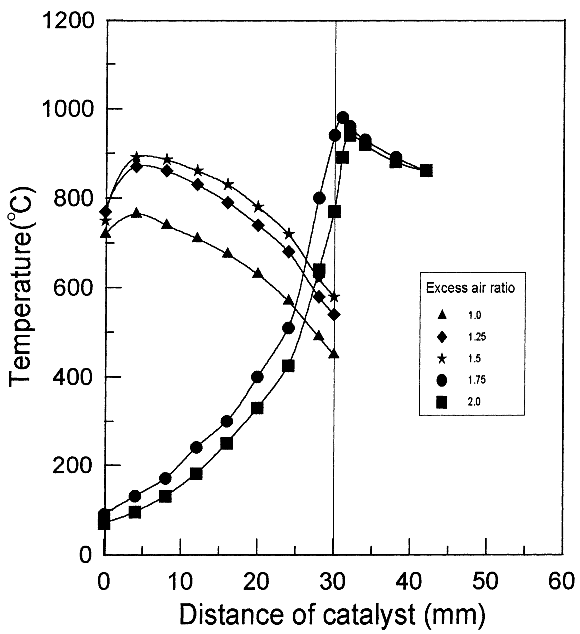

Fig. 5. Temperature distribution of two patterns of catalytic combustion when an igniter is used for starting catalytic combustion. Heat flux: 10.8 kcal/h cm^2; catalyst thickness: 30 mm.

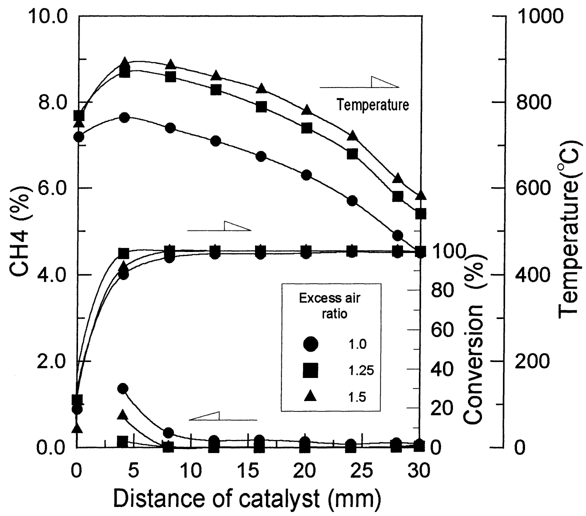

Fig. 6. Methane concentration, conversion and temperature distribution within the catalyst layer as a function of excess air.

catalyst exit. If the excess air ratio exceeded 2.0, the flame was blown off.

It is possible that the patterns of catalytic combustion changed with the amount of heat transferred to the catalyst layer. When the excess air ratio is small, the amount of a mixture entering the catalyst is small, which results in much heat transfer to the catalyst from the flame. As a result the catalyst layer is heated over the light-off temperature at which the catalytic reaction begins. On the contrary, if the excess air ratio is big, the heat transfer to the catalyst is low and the catalyst cannot be heated up to the light-off temperature of the catalyst. These results explain that there exist specific conditions of excess air ratio so as to make the catalytic burner operating on catalytic combustion within the catalyst layer when it is started with an ignition tool.

3.2. *Catalytic combustion characteristics*

Fig. 6 shows the results on methane concentration, conversion and temperature in the catalyst layer for various excess air ratios. The concentration of methane decreases more rapidly and the maximum temperature of the catalyst layer rises as the excess air increases. It is seen in Fig. 6 that the methane concentration is reduced over 95% within 8 mm distance from the catalyst inlet.

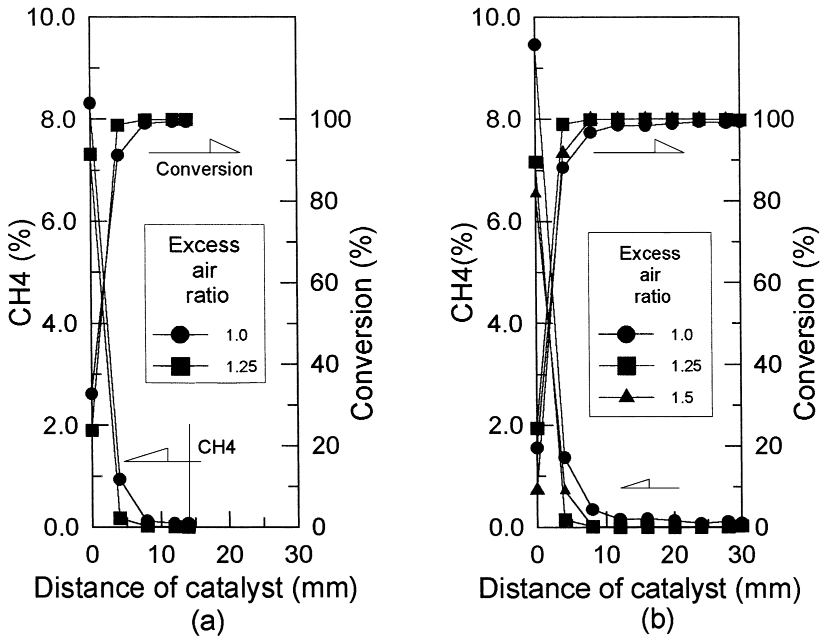

Fig. 7. Methane concentration and conversion vs. catalyst thickness at a heat flux of 10.8 kcal/h cm^2. Catalyst thickness: (a) 15, and (b) 30 mm.

Fig. 7 shows the combustion characteristics with different thicknesses of the catalyst. Fig. 7(a) and (b) are the results of methane concentration and conversion of 15 and 30 mm thick catalysts, respectively. In two cases the reaction of methane is completed within the region of 0–8 mm regardless of the thickness of the catalyst. This means that the thickness of the catalyst should be over 8 mm when we design a catalytic burner.

It is almost mandatory that a catalytic burner has near 100% combustion efficiency. The combustion efficiency of the catalytic burner was measured by analyzing the effluent gas from the catalyst exit. Fig. 8 shows the combustion efficiency of the catalytic burner. At the excess air ratio of 1.0 it is in the range 85–92% depending on the heat flux and it is over 99.5% at an excess air ratio of 1.25 or more. It suggests that the catalytic burner should be operated at an excess air ratio of over 1.25 so as to keep the combustion efficiency over 99.5%.

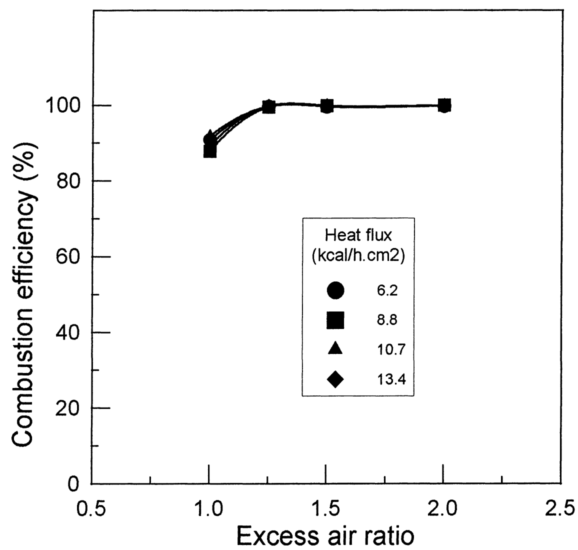

Fig. 8. Effect of the excess air on the combustion efficiency of the catalytic burner at various heat fluxes and the catalyst thickness of 30 mm.

3.3. *Catalytic combustion region*

If the excess air increases more than the proper amount, catalytic combustion is gradually extinguished, since the heat loss from the catalyst layer grows with increasing mixture. This phenomenon is called blow off. When the heat flux decreases excessively, the catalyst could not maintain catalytic

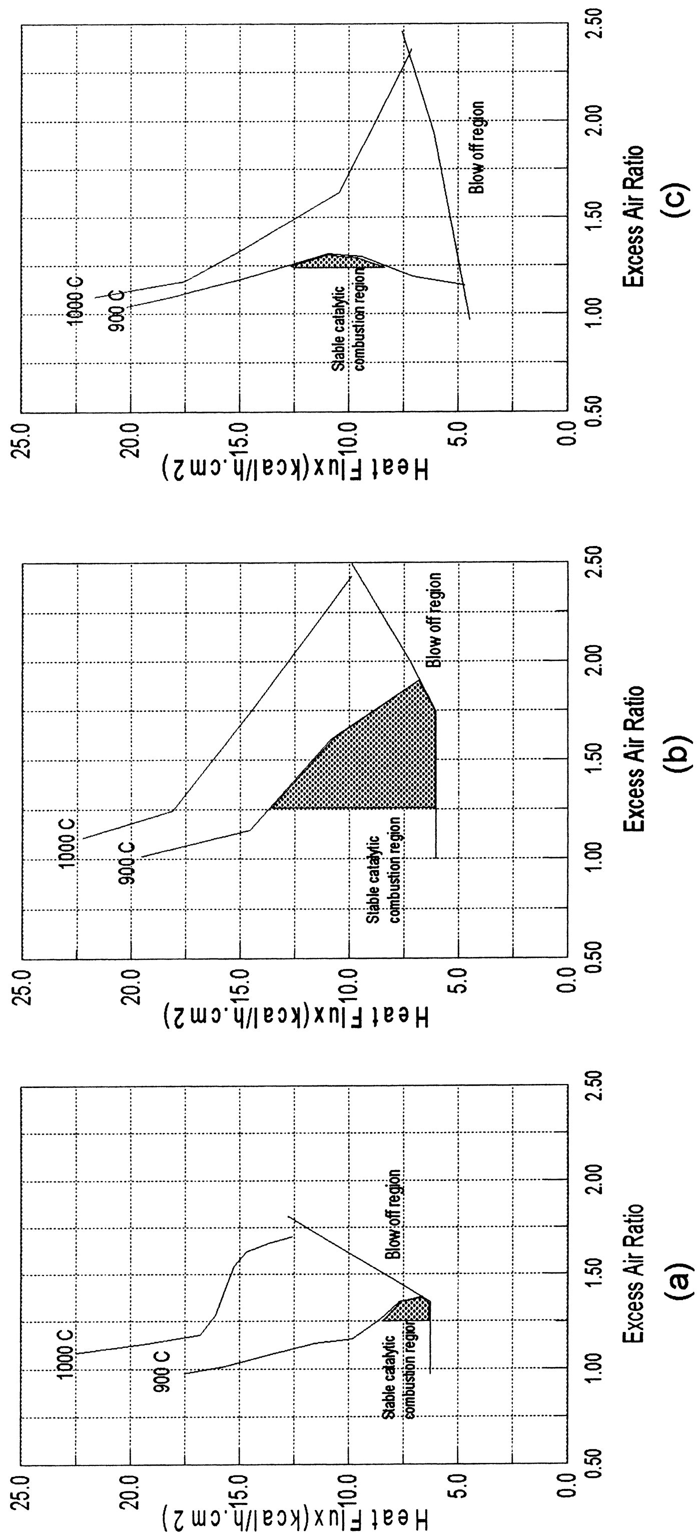

Fig. 9. Variation of catalytic combustion region with various catalytic thickness. Catalyst thickness: (a) 15, (b) 30, and (c) 60 mm.

combustion. It is called low thermal limit. On the other hand, flash back, in which the flame propagates back to the upstream mixture, takes place when the heat flux increases excessively.

To develop a catalytic burner a stable operation condition should be obtained: catalytic combustion can be maintained without blow off, low thermal limit and flash back. Fig. 9 shows results of determination of stable catalytic combustion region obtained under various operation conditions and with catalyst thicknesses. Fig. 9(a), (b) and (c) are results for 15, 30 and 60 mm of the catalyst thickness, respectively. The isothermal line of the maximum temperature of the catalyst layer is also represented in Fig. 9. These temperature data are used to get the safe operation conditions based on the heat-resisting temperature of the catalyst. Within the allowable catalytic combustion region the combustion efficiency must be more than 99.5%. The shaded region in Fig. 9 represents the stable catalytic combustion region. In this region the maximum temperature of the catalyst layer is less than 900°C, the combustion efficiency is over 99.5% and there is no blow off and no flash back. These results can be used as data for designing the catalytic burner.

It is found that the stable catalytic combustion region markedly depends on the catalyst thickness. The 15 and 60 mm thick catalyst, show the shallow region of the stable catalytic combustion due to the fast cooling effects for the former and the thermal storage effects for the latter, respectively.

It is desirable to make stable the catalytic combustion region as large as possible for developing a catalytic burner. The larger it becomes, the bigger the range of heat flux and the excess air ratio. As shown in Fig. 9, the 30 mm thick catalyst is thought to be the best with the excess air ratio of 1.25–1.75 and a heat flux of 7–14 kcal/h cm^2.

4. Conclusions

A study for developing a catalytic burner was carried out. The catalyst was the noble metal Pd/NiO supported on honeycomb (400 cells/$in.^2$) wash-coated with promoted γ-Al_2O_3. Temperature and catalytic combustion characteristics, and catalytic combustion region were analyzed. These results are as follows:

1. The temperature of the catalyst layer rose rapidly near the catalyst inlet and then fell down slowly. As the excess air ratio grew, the maximum temperature increased and its position moved toward the catalyst exit.
2. When the catalytic burner was started by the igniter on the catalyst surface, two patterns of catalytic combustion occurred depending on the excess air ratio. The catalytic combustion was completed within the catalyst layer for an excess air ratio of 1.0–1.5 and flame combustion took place for an excess air ratio of 1.75–2.0.
3. Over 95% catalytic methane conversion proceeded within 8 mm distance from the entrance of the catalyst regardless of the catalyst thickness. The combustion efficiency of the catalytic burner reached more than 99.5% at an excess air ratio of over 1.25.
4. The stable catalytic combustion region with a 30 mm thick catalyst was obtained under the following operation conditions: combustion efficiency, 99.5%; excess air ratio, 1.25–1.75; heat flux, 7–14 kcal/h cm^2.

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