CATALYTIC COMBUSTION OF HYDROGEN—II. AN EXPERIMENTAL INVESTIGATION OF FUNDAMENTAL CONDITIONS FOR BURNER DESIGN

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Abstract—The performance of catalysts in different forms was investigated for the design of a catalytic combustor with hydrogen fuel. The catalysts tested had dimensions of 150 × 150 mm, and consisted of a ceramic honeycomb impregnated with Pt, two Ni metal foams coated with Pd powder which differed from each other in pore size, and a ceramic foam coated with Co-Mn-Ag oxide powder. In the diffusive mode of operation, the Pd-coated Ni foam with larger pores exhibited the highest combustion efficiency. The ceramic foam with the oxide coating also provided smooth hydrogen combustion in the range 0.2-1.0 kcal cm⁻² h⁻¹. Combustion efficiency was improved by increasing the amount of premixed air and totally supplied air. Spot measurements of surface temperature and gas composition were carried out over the catalyst surface and the characteristic features of each catalyst were compared and discussed.

INTRODUCTION

Previous work in this series has shown the results of catalyst screening for low-temperature catalytic combustion of hydrogen [1]. It has been found that several inexpensive oxides of 3d transition metals, as well as platinum-group metals and their oxides, are active at intermediate temperatures around 150°C and that palladium metal supported on silica gel can initiate hydrogen combustion even at temperatures below 0°C.

The present investigation was undertaken to see what catalyst structure is suitable for a catalytic burner with hydrogen fuel. Although the use of catalytic combustion in heating appliances has invoked much interest [2-7], little attention has been paid to the effect of the catalyst shape on the performance of a catalytic heater.

Development of practical catalytic heaters requires the determination of optimum construction and the knowledge of operating properties. The shape of a catalyst body is assumed to be one of the major factors affecting the performance of a catalytic heater, because distribution of fuel over the catalyst body and diffusion of air to its surface against the bulk flow of fuel controls the operating properties in the diffusive mode of operation.

In most commercial and prototype catalytic space heaters [2-5, 8], asbestos wool, ceramic wool, fiberglass or an aluminium sheet is used to support the catalyst. Unfortunately, information on the effect of catalyst structure is incomplete and no type of catalyst body other than a fibrous pad and a metal plate impregnated with platinum-group metals seems to have been used for a diffusive catalytic heater.

Therefore, four types of catalysts (all non-fibrous) were tested. Their operating properties are described and discussed in the present investigation.

EXPERIMENTAL

The performance tests of four catalysts (dimensions 150 × 150 mm) were carried out using 99.99% pure hydrogen and the apparatus shown in Fig. 1. A ceramic wool mat adapted to facilitate uniform dispersion of hydrogen was disposed opposite the front side of the catalyst. Combustion air dried by silica gel was fed to a premixing chamber concurrently through two tubes and to a gas outlet chamber tangentially through four tubes. Spot temperature and spot composition of gas mixtures on the front surface of the catalysts were measured with nine chromel-alumel thermocouples connected to a digital multi-temperature recorder (Yokogawa Electric Works Ltd., Type 3874) and with nine microprobes for gas sampling connected to a gas chromatograph (Yanaco, Model G1800). The local spots for both temperature and gas composition measurements were numbered as shown in Fig. 1.

Fig. 1. Schematic diagram of catalytic combustion apparatus. A, ceramic wool mat; B, catalyst body; C, thermocouple; D, gas sampling probe.
Table 1. Catalysts used in performance tests

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst material</th>
<th>Preparative method</th>
<th>Dimensions (l x w x d) (mm)</th>
<th>H₂ comb. eff. at 1.2 kcal cm⁻² h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₂*</td>
<td>Pd Ni foam No. 2⁺</td>
<td>Coating of Pd</td>
<td>150 x 150 x 5</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>(11-15 cells inch⁻¹)</td>
<td>fine powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₂*</td>
<td>Pd Ni foam No. 5⁺</td>
<td>Coating of Pd</td>
<td>150 x 150 x 5</td>
<td>88.4</td>
</tr>
<tr>
<td></td>
<td>(35-44 cells inch⁻¹)</td>
<td>fine powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T₄⁺</td>
<td>Pt Ceramic honeycomb</td>
<td>Pt was impregnated from its HCl solutions</td>
<td>150 x 150 x 25</td>
<td>87.5</td>
</tr>
<tr>
<td></td>
<td>(14 cells inch⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G₈</td>
<td>Co–Mn–Ag oxide, 20:4:1 (atomic ratio)</td>
<td>Coating of oxide powder</td>
<td>150 x 150 x 5</td>
<td>93.0</td>
</tr>
</tbody>
</table>

* Available from Daido Steel Co. Ltd. (Japan).
† Available from Sumitomo Electric Co. Ltd. (Japan).
‡ Available from Tanaka Precious Metals Industry Ltd. (Japan).
§ Active oxides developed by our laboratory. Further details will be published in a subsequent paper.
ǁ Available from Bridgestone Co. Ltd. (Japan).

The combustion efficiency of hydrogen and the equivalent ratio of air at the catalyst surface were determined by analysing the concentration of hydrogen, oxygen and nitrogen with a gas chromatograph. Since water was the only product of combustion and was absorbed by silica gel before a sampled gas was injected into the gas chromatograph, the efficiency of hydrogen combustion was defined as:

Hydrogen combustion efficiency (E)

\[
E = \frac{(1 - \text{hydrogen slippage}) \times 100\%}{\frac{[\text{N}_2]}{[\text{O}_2] + \frac{1}{2}[\text{H}_2]} \times 100\%}
\]

(1)

where \([\text{N}_2] \), \([\text{O}_2] \) and \([\text{H}_2] \) are concentrations by volume % of nitrogen, oxygen and hydrogen, respectively.

The equivalent ratio of combustion air to all supplied fuel was defined as:

Equivalent air ratio (\(\lambda\))

\[
\lambda = \frac{1}{1 + 1.88 \frac{[\text{H}_2]}{[\text{N}_2]} - 2 \times 1.88 \frac{[\text{O}_2]}{[\text{N}_2]}}
\]

(2)

Heat inputs were inferred from the calorific value of hydrogen and the gas flow rates, which were measured by rotameters fully calibrated over the range of experiments. Table 1 gives a list of the catalyst bodies examined, with a brief description of each and the efficiency of diffusive hydrogen combustion at a specific heat input of 1.2 kcal cm⁻² h⁻¹.

RESULTS AND DISCUSSION

Time course of catalyst surface temperature

Surface temperatures of the catalyst bodies are dependent on heat input, type of catalyst body, location on the catalyst body, amount of air supplied and operation duration. Figs. 2 and 3 show how the catalyst surface temperatures on the top and bottom of the catalyst body change with time of operation and how they are dependent on the amount of air supplied and type of combustion, i.e. diffusive or completely premixed combustion.

After self-starting from room temperature, the surface temperature rose more rapidly on the metal foam catalyst D₂ than on the ceramic honeycomb catalyst Th. For both catalysts under diffusive operation, at least 30 minutes were required to reach the steady state and
the spot temperature was higher at the vertically lower position of catalyst (No. 8) than at the higher position (No. 2) with air below the stoichiometric ratio. With air over the stoichiometric amount, this temperature distribution was reversed.

An increase in secondary air from an equivalent ratio of 0.8 to 1.0 may cause a drastic change in the distribution of hydrogen and combustion air over the catalyst surface. At a low air ratio, it was probable that the distribution of air was localized on the bottom of the catalyst body due to its specific gravity being remarkably larger than that of hydrogen. Therefore, combustion of hydrogen may take place predominantly over the lower part of the catalyst. When a stoichiometric amount of air was supplied, it could also be distributed to the upper part of the catalyst. As hydrogen was assisted to flow upward through the catalyst body by an air stream, combustion at the top predominated.

In completely premixed combustion, at any ratio of air, the spot temperatures were always higher at the top than at the bottom. The temperature difference between the top and bottom of the catalyst body was considerably larger for the catalyst D2, which was composed of three-dimensionally distributed macropores. Over this catalyst, the mixed gas could flow upward along with temperature gradient and burn at the top. This may lead to a further rise in temperature at the top. On the other hand, vertical flow of the gas mixture was inhibited over the honeycomb-type catalyst by the two-dimensionally arranged channels. Absence of vertical flow could account for the relatively small temperature difference between the top and bottom of the catalyst.

On the ceramic honeycomb, surface temperature continued to change with time for a long time, especially in premixed combustion. However, as shown in Fig. 3, in experimental runs carried out after the run at a larger heat input or larger air ratio, surface temperature reached a steady state in a short time. The combustion efficiencies shown in Figs. 6 and 7 were obtained at the end of each run. They varied only slightly with time after 30 min although surface temperature was still changing to some extent.

Fig. 4 shows the spot surface temperature on the centre of the catalysts in diffusive combustion as a function of operation duration. Since a sufficient amount of air with an equivalent ratio of about 1.5 was supplied, the temperature rose rapidly on initiation of combustion and reached nearly constant values within 20 min, except for the ceramic honeycomb catalyst. The steady-state temperatures changed with heat input but were almost independent of the type of catalysts. By taking the time variation shown in Fig. 4 into consideration, the following spot measurements of catalyst temperature and gas composition were performed after 1 h operation.

Effect of total amount of air supplied

Figs. 5 and 6 show the effect of the amount of air supplied to the chambers on the combustion efficiency of hydrogen. The dotted line (---) shows the theoretically obtainable combustion efficiency. It was found that, at a heat input as low as 0.4 kcal cm\(^{-2}\) h\(^{-1}\),...
diffusive combustion yielded a higher combustion efficiency than premixed combustion over the nickel foam catalyst (D3) and the ceramic honeycomb catalyst (Tb).

The above unexpected results can be interpreted by taking into consideration the observed difference in catalyst temperature shown in Figs. 2 and 3. Premixed combustion at a low heat input lowers the catalyst temperature due to rapid removal of heat released by combustion, and therefore results in lower combustion efficiency. On the other hand, the combustion efficiency in diffusive combustion appeared to be largely affected by the extent of mixing hydrogen with air over the catalyst surface. Since the flow rate of hydrogen passing through the catalyst body was moderate enough at a low heat input for the ambient air to approach the catalyst surface, the resulting long residence time accompanied by high catalyst temperature yielded a high combustion efficiency of hydrogen.

In the heat input range above 0.8 kcal cm\(^{-2}\)h\(^{-1}\), premixed combustion was advantageous over diffusive combustion, as typically shown in Fig. 6. It is worth noting that the nickel metal foam support with larger pore size offered a higher combustion efficiency than the one with smaller pore size in diffusive combustion.

Fig. 6 shows detailed features of the operating properties of catalyst D5 in diffusive combustion at 1.2 kcal cm\(^{-2}\)h\(^{-1}\). At this heat input, overall combustion efficiency was not as high, however, it increased with an increase in the amount of secondary air supplied. The low overall efficiency was mainly due to the spot combustion efficiency at the upper position of the catalyst where the entrainment of air was limited to a stoichiometric amount. Variation of spot catalyst temperature with the amount of secondary air showed a characteristic feature: that temperature at the bottom (No. 9) dropped with an increase in secondary air while it appreciably rose at the top (No. 1). At the bottom, the spot temperature tended to fall due to dilution by an excessive amount of air diffusing from the ambience. On the other hand, at the top, the amount of air entrained at the catalyst surface was only slightly increased with increasing secondary air. However, the slight increase in the entrained air markedly improved the spot combustion efficiency and raised the spot surface temperature.

**Effect of premixing hydrogen with air**

Since the flow of air to the catalyst surface from the ambience appeared to control the performance of a diffusive catalytic burner, partial premixing with air was expected to be effective, especially at a high heat input, for the improvement of combustion efficiency. Fig. 8 shows the results of such experiments for the catalyst Tb. The overall combustion efficiency increased appreciably with an increase in the amount of premixed air. However, the surface temperature of the catalyst
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Fig. 9. Effect of premixing air on operating properties of catalyst D2. ○, Overall combustion efficiency of hydrogen. Heat input, 1.6 kcal cm\(^{-2}\) h\(^{-1}\). Equivalent ratio of totally supplied air, \(\lambda = 2.3\).

dropped when the equivalent ratio of premixed air was increased from 0.4 to 0.6. This implies that with an increase in premixed air, the gas mixture passes through the catalyst body at a higher rate and removes the heat released at the catalyst body more rapidly.

In the catalytic combustion of methane [2], the premixing effect was largely offset by convective cooling due to an increase in rate of flow of gas mixture, and addition of the air to 50% stoichiometry caused an appreciable fall of the overall combustion efficiency. In contrast to methane, as hydrogen is a readily oxidizable fuel, the convective cooling did not cause a fall in the overall combustion efficiency.

Figs. 9 and 10 show the results of partially premixed combustion over the catalysts D2 and G0, respectively. The spot combustion efficiency was increased most appreciably at the upper position, and therefore the overall efficiency was significantly improved. Partial premixing was most effective on the oxide catalyst G0 for the improvement of overall efficiency. The efficiency was improved from 88 to 98% by premixing air to a 40% stoichiometric amount.

Effect of heat input

Fig. 11 shows the dependence of the combustion efficiency of hydrogen on heat input in diffusive operation for the four catalysts. The efficiency decreased gradually with increasing heat input over the Pt-impregnated ceramic honeycomb (Th), while it fell sharply at a heat input of 1.2 kcal cm\(^{-2}\) h\(^{-1}\) over the Pd-coated Ni metal foam which had a smaller porosity (D2). It is worth noting that the Ni metal foam support with larger pores (D2) offered a higher efficiency than the one with smaller pores (D3) at high heat ratings. The structure and the size of pores may have a predominant role in determining the combustion efficiency at high ratings.

A different feature was observed for the ceramic foam coated with oxide catalyst (G0): the efficiency was a parabolic function of heat input and therefore the usable limit of heat input has to be imposed on both the upper and lower sides. The oxide catalyst developed in our laboratory was much more active than any other conventional oxide catalyst, however, it was still not sufficiently active at lower heat ratings where temperature remained at around 50°C on the most of the catalyst body.

According to the present European standards for LPG heaters, which requires fuel slippage of less than 4%, the adjustable range of heat input for hydrogen is from 0 to 1.4 kcal cm\(^{-2}\) h\(^{-1}\) with the nickel foam coated with Pd fine powder (D2).

Fig. 10. Effect of premixing air on operating properties of catalyst G0. ○, Overall combustion efficiency of hydrogen. Heat input, 1.6 kcal cm\(^{-2}\) h\(^{-1}\). Equivalent ratio of totally supplied air, \(\lambda = 1.73\).

Fig. 11. Dependence of combustion efficiency of hydrogen on heat input in diffusive combustion. Equivalent ratio of secondary air, \(\lambda_s = 1.8 \pm 0.2\).
Difference in temperature distribution over catalyst surface

Temperature at nine spots on the catalyst surface was continuously measured. In Fig. 12 the steady-state temperature at the three representative spots is shown as a function of heat input. Significant differences were observed in the temperature distribution between ceramic honeycomb, metal foam and ceramic foam supports. The ceramic honeycomb ($T_h$) had the most uniform temperature distribution, while Ni metal foam with larger porosity ($D_2$) had considerably non-uniform distribution. Although catalyst $D_2$ offered the highest combustion efficiency, this non-uniform temperature distribution would impose a limit on operating at higher heat ratings because of flame ignition at a local hot spot.

The temperature difference between the upper and lower spot became more remarkable with increasing heat input over the catalyst $D_2$, while it became less appreciable over the other three catalysts. Over the catalysts $G_0$ and $D_2$, the temperature at the upper spot was exceeded by the temperature at the lower spot at a high heat input. This indicates the change in the local heat rating with an increase in hydrogen feed rate. The upward flow of hydrogen and air across catalysts with relatively small pores was restricted, as observed in Fig. 14. The lack of entrained air may reduce the combustion efficiency. Therefore, an increase in overall heat input did not necessarily bring about higher spot heat rating at the top of the catalysts. On the other hand, with appropriately large pores of three-dimensional distribution (e.g. catalyst $D_2$) an increase in overall heat input led to higher heat rating at the top of the catalyst body due to the ease of upward flow of air through pores.

Measurements of spot ratio and spot combustion efficiency

Spot measurements of the concentrations of hydrogen, oxygen and nitrogen were made on nine spots over the catalyst surface, and air ratio and combustion efficiency at each spot were determined. Fig. 13 shows the spot equivalent ratios of diffusive air as a function of heat input. The equivalent air ratio on the top of each catalyst had a declining tendency with an increase in heat input. Especially, over the catalyst $D_2$ (with small pores) the local equivalent ratio of diffusive air at the top was below a stoichiometric amount even at moderate heat ratings. Considering the local spot air ratio in connection with combustion efficiency shown in Fig. 11, it can be suggested that catalysts with higher spot air ratios, such as $D_2$ and $G_0$ could offer higher combustion efficiency in diffusive combustion.

Fig. 14 schematically represents the distribution of the catalyst surface temperature, the equivalent ratio of entrained air, and the efficiency of hydrogen combustion over the four catalysts. Surface temperature was of uniform distribution and mostly between 150°C and 200°C on catalysts $T_h$ and $G_0$ at a heat input of 1.2 kcal cm$^{-2}$ h$^{-1}$. As described above, the catalyst structure has a great influence on the temperature distribution, however, it can also be pointed out that ceramic supports are advantageous over metal supports in providing a uniform temperature distribution. The surface temperature was markedly non-uniform on catalyst $D_2$. Temperature at the top was over 300°C, while it was as low as ca 110°C at the bottom. The temperature distribution over catalyst $D_2$ presented a clear contrast to that of the other three catalysts. Because of the lack of air flowing into the catalyst body...
and the difficulty of upward flow of air through the catalyst, the bottom of the catalyst was warmer than the top.

Spot equivalent ratio of entrained air and spot combustion efficiency decreased with vertical height. Deficiency in the entrained air considerably reduced the combustion efficiency at the top of the catalysts except for D2. A similar feature, that spot combustion efficiency varied only slightly, was observed on catalysts Th and D2. However, the temperature distribution was in marked contrast to each other. It can be assumed from the uniform distribution of surface temperature that hydrogen was distributed uniformly over catalyst Th. The markedly high temperature at the top of catalyst D2 indicated the localization of hydrogen brought about by the upward flow through large pores, of three-dimensional distribution.

It can be concluded that sufficient entrainment of air
Fig. 15. Effect of heat input on operating properties of catalyst $D_s$ in perfectly premixed combustion. Overall combustion efficiency. Equivalent ratio of primary air, $\lambda_i = 1.5 \pm 0.15$.

It is presumable that the adjustable heat input could be extended to much larger values than 1.6 kcal cm$^{-2}$ h$^{-1}$, because shorter residence time, resulting from an increase in heat input, could be compensated by a temperature rise of the catalyst body. Moreover, as clearly observed in Fig. 16, temperature distribution was more uniform in premixed combustion than in diffusive combustion. Therefore, completely premixed combustion can be sustained over a wide range of heat rating without ignition at a local hot spot.

CONCLUSION

The present experimental study has focussed on the effect of fundamental conditions of hydrogen fuelled catalytic burners on their operating properties. In diffusive combustion, Pd-power coated Ni foam with relatively large pores could offer the highest combustion efficiency, however, it suffered from considerable non-uniform distribution of surface temperature. It was demonstrated that a ceramic foam coated with Co-Mn-Ag oxide, developed in our laboratory was practically utilisable for catalytic appliances operating on hydrogen fuel, although it required a little preheating for initiating combustion. Premixing of air to a 40% stoichiometric amount with hydrogen was effective in improving combustion efficiency. In completely premixed operation, combustion efficiency higher than 99% was obtained in the heat input range up to 1.6 kcal cm$^{-2}$ hr$^{-1}$.

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REFERENCES

8. Notice d'utilisation de radiateurs BUTA THERM’X (France).