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Development of a high-temperature combustion catalyst system and prototype catalytic combustor turbine test results

H. Sadamori [a,*], T. Tanioka [b], T. Matsuhisa [c]

[a] Research and Development Center, Osaka Gas Co., Ltd., 6-19-9 Torishima, Konohana, Osaka 554, Japan
[b] Polymer and Chemical Technology Research Laboratory, Kobe Steel, Ltd., 1-5-5 Takatsukadai, Nishi, Kobe, Hyogo 651-22, Japan
[c] Shimonoseki Factory, Catalysts and Chemicals Inc., Far East, 7-2-10 Sako, Hikoshima, Shimonoseki, Yamaguchi 750, Japan

Abstract

A new combustion catalyst system for gas turbines composed of high-temperature durable ceramic catalysts made of fine manganese-substituted hexaaluminate particles and noble metal-carrying cordierite honeycomb catalysts has been developed. A 160 kW prototype catalytic combustor turbine rigged with a 220 mm in diameter catalyst system was constructed and tested including a continuous 215-hour operation and repeated sudden stops. The results showed practical combustion performance with ultra-low NO_x emissions less than 40 ppm (converted to 0% oxygen) and the feasibility of long term catalyst durability.

Keywords: Combustion; Gas turbines; High temperature combustion

1. Introduction

A low cost, ultra-low NO_x catalytic combustor is now in demand to popularize gas turbine cogeneration systems. The greatest technical challenge facing the catalytic combustor is the development of a 1000 to 1200°C-durable combustion catalyst. We have been wrestling with this difficulty while developing new ceramic combustion catalysts made of manganese-substituted hexaaluminate invented by Arai et al. [1]. Since the ceramic catalysts are expected to have 10 000 hours or more of activity life at 1300°C, the main issues for their practical use are how to overcome the drawbacks of their low thermal shock resistance and high ignition temperature.

* Corresponding author.

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2. Concept of the catalytic combustor for gas turbines and our target

Fig. 1 shows the schematic construction of the catalytic combustor we intend to develop. The chief feature of this combustor is that the main combustion occurs within the honeycomb-shaped combustion catalyst layer, scarcely producing NO_x at a temperature that is higher than the required turbine inlet temperatures. A precombustor at the foremost part constructed of a conventional flame burner is used for the engine start-up and for pre-heating the inlet air to about 450°C in steady-state operation. The air bypass valve at the back of the catalyst is used for optimum combustion control according to performance variations of the engine. Since the total NO_x emissions from this combustor are controlled by those from the precombustor, the combustion catalyst system

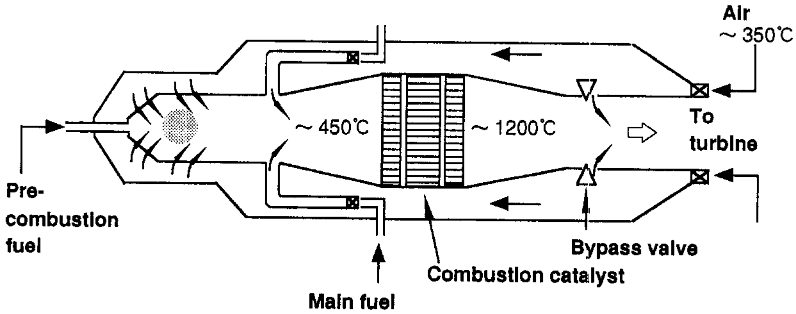

Fig. 1. Schematic construction of the catalytic combustor.

Table 1
Targets of the catalytic combustor

Items	Targets
Applied turbine	
Capacity	1000–1500 kW
Max. inlet temp.	1100°C
Pressure	10 atm, abs.
NO_x emissions	< 40 ppm(0% O_2)
Combustion efficiency	> 99%
Pressure loss ratio	< 5%
Catalyst life	> 8000 h, > 400 cycles
Fuel	Natural gas

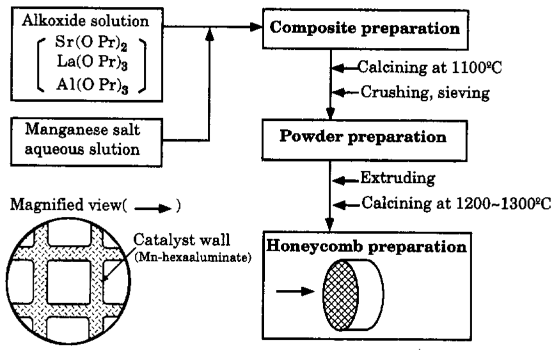

Fig. 2. Preparation method for the ceramic combustion catalysts.

must not only have high-temperature durability but also a low ignition temperature for combustion. Table 1 shows our targets for gas turbine catalytic combustors.

3. Development of ceramic combustion catalysts and the catalyst holder

Fig. 2 shows the preparation method for ceramic combustion catalysts made of $Sr_{0.8}La_{0.2}MnAl_{11}Al_{19-\alpha}$. In the first step, the composite is prepared by the alkoxide method. In the second step, it is turned into powder by calcining at 1100°C, crushing, and sieving. In the last step, the ceramic combustion catalyst is prepared by extruding into a honeycomb shape after kneading the mixture of the powder, water, and some organic binders and by calcining at 1200 or 1300°C. Since the ceramic catalysts are composed of uniform manganese hexaaluminate, they are free from crucial deactivation factors, namely the catalyst coat breaking off or catalyst components reacting with the honeycomb substrate as on conventional coated type combustion catalysts. However, their thermal shock resistance is low because of their high thermal expansion ratio and low mechanical strength shown in Table 2, compared with conventional cordierite honeycombs, which are mostly used as the substrate for combustion catalysts. Therefore, their problem in application is how to overcome their low thermal shock resistance.

Table 2
Physical properties of the ceramic combustion catalysts

Properties	1200°C-calcined sample	1300°C-calcined sample
Bending strength ($MN \cdot m^{-2}$)	13.30	28.04
Young modulus ($GN \cdot m^{-2}$)	8.753	16.03
Thermal expansion ratio ($°C^{-1}$)	8.8×10^{-6}	8.8×10^{-6}

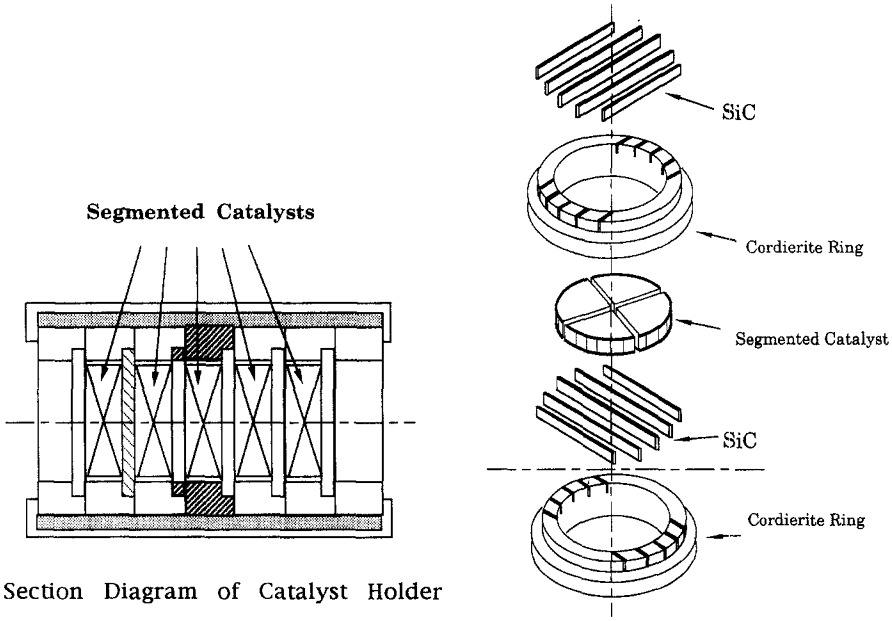

Fig. 3. Catalyst holder.

To solve this problem we have developed the catalyst holder shown in Fig. 3, in which segmented ceramic catalysts are loosely packed both in the axial direction and in the radial direction, and the stresses in the catalysts are greatly reduced. We have also developed a thermal stress analysis method by which thermal stresses generated in the honeycomb during the operation can be simulated. The details are described in another paper presented at this Workshop [2]. We designed 220-mm in diameter ceramic combustion catalysts whose surfaces were segmented into twelve pieces to prevent crack generation for the turbine tests by this analysis method.

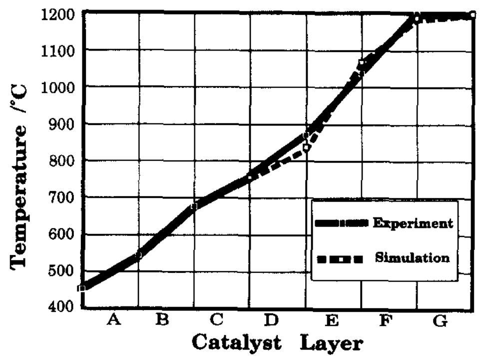

Fig. 4. Axial gas temperatures within the catalyst in natural gas combustion at 10 atm.

4. Development of a combustion catalyst system and its performance

Another drawback of the ceramic combustion catalysts is that their ignition temperature is higher than 600°C. To overcome this drawback, we have developed the catalyst system shown in Table 3 composed of noble metal-carrying cordierite honeycomb catalysts in the front stages, 1200°C-calcined ceramic catalysts in the middle stages, and 1300°C-calcined ceramic catalysts in the back stages. Fig. 4 shows a measurement result of the axial gas temperatures within the catalysts system in the steady state of natural gas combustion at 10 atm. The experiment was performed using a 50-mm diameter catalyst system, natural gas (composition: 88% CH_4, 6% C_2H_6, 4% C_3H_8, 2% C_4H_{10}, sulfur compounds 7 mg S/Nm^3), and air preheated by an electric heater. The catalyst inlet temperature, the theoretical adiabatic combustion temperature, and the reference velocity (catalyst inlet velocity at 450°C and 10 atm) were 450°C, 1200°C, and 9 m/s, respectively. It is noted that the outlet temperature of noble metal-carrying catalysts is below 800°C, with long term durability, and that of the ceramic catalyst at the final stage reaches about 1200°C, equal to the theoretical adi-

Table 3
Combustion catalyst system for gas turbines

Stage	Kind of catalyst	Cell number (cpi)	Height (mm)
A, B, C	Noble metal-carrying cordierite honeycomb	200	20×3
D, E	Mn-substituted hexaaluminate ceramic honeycomb calcined at 1200°C	300	20×2
F, G	Mn-substituted hexaaluminate ceramic honeycomb calcined at 1300°C	300	20×2

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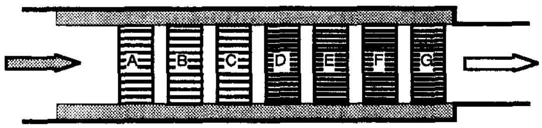
D E	Mn substituted hexaaluminate ceramic honeycomb calcined at 1200℃	300 cpi	20mm×2
F G	Mn substituted hexaaluminate ceramic honeycomb calcined at 1300℃	300 cpi	20mm×2



abatic combustion temperature of the inlet gas mixture. It was found that the combustion efficiency expressed by the complete oxidation rate was more than 99.9% and that NO_x emissions converted to 0% oxygen were almost zero by the exhaust gas analysis. Fig. 4 also profiles the numerical analysis results on combustion phenomena within the honeycomb passage based on the catalytic oxidation rates of the ceramic catalysts measured with a microreactor and a homogeneous oxidation rate quoted from the literature. The two profiles agree fairly well. The details of the analysis method are described in another paper presented at this Workshop [3].

5. Prototype catalytic combustor turbine tests

We have prepared a 160 kW prototype catalytic combustor turbine test device rigged with a 220 mm in diameter segmented catalyst system in cooperation with Kawasaki Heavy Industries, Ltd. The catalyst system in which the ceramic catalysts were segmented into twelve pieces in the radial direction, had the same configuration as that of Table 3 in the axial direction and was held as Fig. 3. Fig. 5 shows the schematic construction of the test device. The catalytic combustor construction is similar to that in Fig. 1. The nominal turbine pressure ratio, air flow rate, and combustor inlet air temperature under standard conditions are 8.5, 1.8 kg/s, and 350°C, respectively. The engine load was adjusted by an eddy current dynamometer. The operations related to the catalyst inlet temperature, the engine load, the air bybass valve, and the engine speed were manually controlled, while the fuel flow rates were automatically controlled according to the engine speed. The precombustion and main fuel flow rates were measured by orifice meters, respectively. The catalyst inlet and outlet temperatures were measured at four points by 3.2

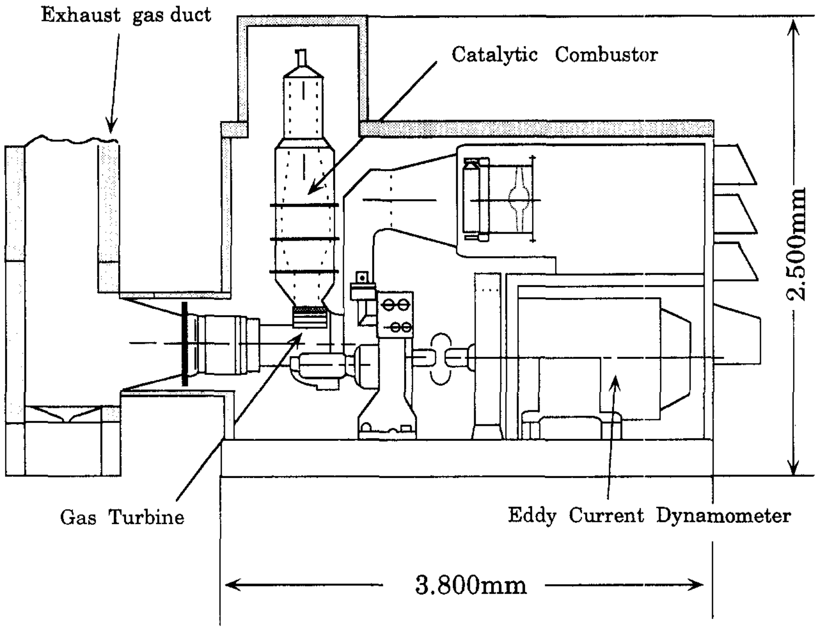


Fig. 5. Schematic construction of the catalytic gas turbine test device.

mm in diameter sheathed thermocouples, respectively. The catalyst temperatures within the holder were measured at twenty seven points by 1 mm in diameter sheathed thermocouples. The exhaust gas from the turbine was analyzed by a FID-total hydrocarbon meter, a NDIR-CO/CO_2 meter and a chemi-luminescence NO_x meter. The opening, in degrees, of the air bypass valve was estimated from the driving voltage of the device. Natural gas whose compositions was described above was used as fuel.

5.1. Engine start-up in the precombustion mode

The engine was started up by using pressurized external air, an engine starter, and the precombustion burner under the condition of no load and air bybass valve closed. Fig. 6 shows the axial temperature variations of the catalyst layer in the engine start-up operation. It can be seen that the engine start-up time was about one minute and that the peak temperature of the catalyst was about 1100°C.

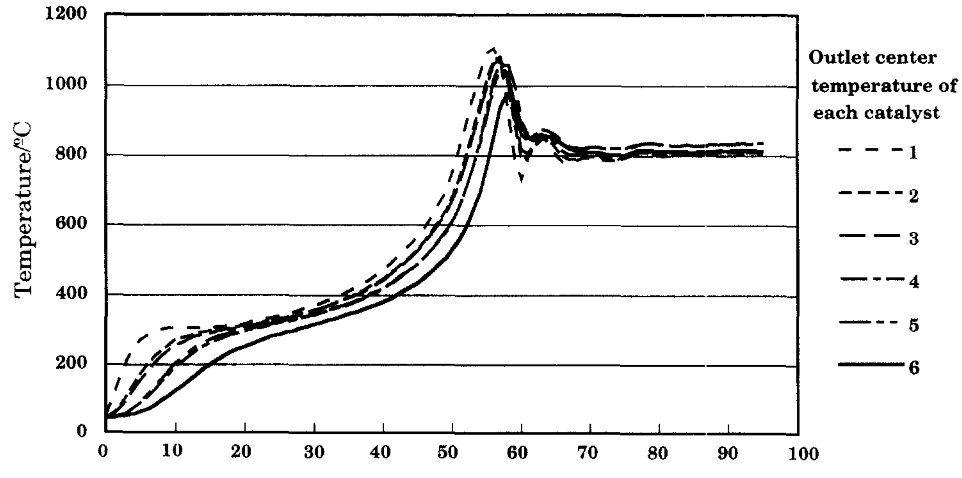


Fig. 6. Catalyst temperature variations in the engine start-up operation.

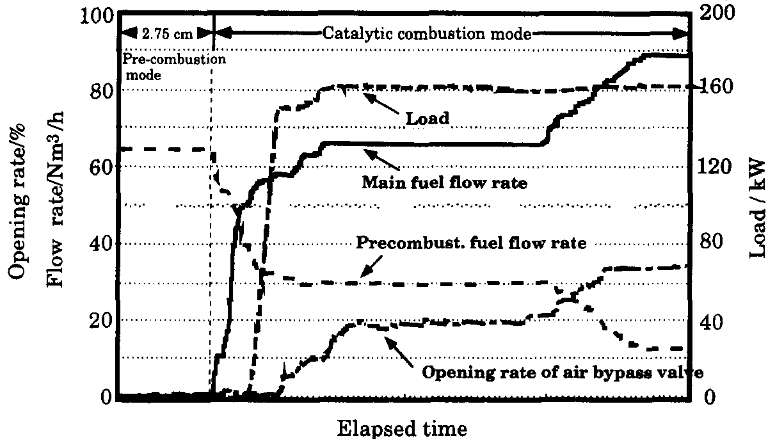


Fig. 7. Variations of fuel flow rates, the engine load, and the opening, in degrees, of the air bypass valve during the mode transfer.

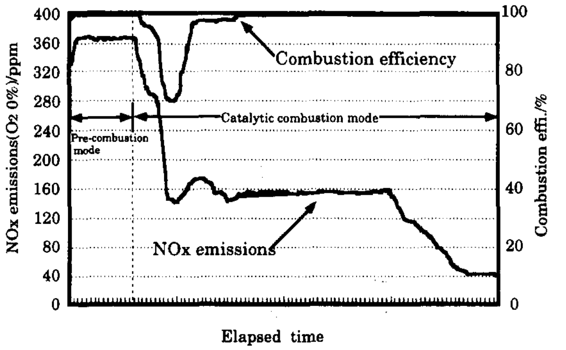


Fig. 8. Variations of the combustion efficiency and NO_x emissions during the mode transfer.

Table 4
Catalytic combustor performance in the steady state operation

Conditions		Results	
Turbine load	163.3 kW	Mean catalyst outlet temp.	1086°C
Compressor inlet air temp.	15.9°C	Exhaust gas composition	
Combustor inlet air temp.	368°C	Total hydrocarbons	3 ppm
Combustor inlet pressure	8.62 atm	Carbon monoxide	< 1 ppm
Mean catalyst inlet temp.	458°C	NO_x	9.4 ppm
Preheating fuel flow rate	13.0 Nm^3/h	Carbon dioxide	2.292%
Main fuel flow rate	89.5 Nm^3/h	Oxygen	16.52%
		Combustion efficiency	44.2%
		Pressure loss ratio	4.17%

5.2. Tests in the catalytic combustion mode

The transfer from the precombustion to the catalytic combustion mode was performed by reducing the precombustion fuel flow rate and increasing the catalytic combustion fuel flow rate with the air bypass valve still closed while keeping the engine speed constant.

When the catalyst inlet temperatures were lowered to be about 550°C, the engine was loaded to the rated value. Immediately after, the air bypass valve was gradually opened until a combustion efficiency (based on calorific values) higher than 99% was attained. After a while, the mode transfer was again continued until NO_x emissions less than 40 ppm (converted to 0% oxygen) were attained. Fig. 7 shows the variations of the precombustion and the catalytic combustion fuel flow rates, the engine load, and the opening, in degrees, of the air bypass valve during the mode transfer. Fig. 8 shows the variations of the combustion efficiency and NO_x emissions during the mode transfer. The combustion efficiency initially decreased to about 70% but increased to more than 99% soon after, while NO_x emissions decreased from 360 ppm in the precombustion mode to less than 40 ppm in the steady-state catalytic combustion mode. Table 4 summarizes the catalytic combustor performance in the steady state. It is noted that the target values for NO_x emissions, combustion effi-

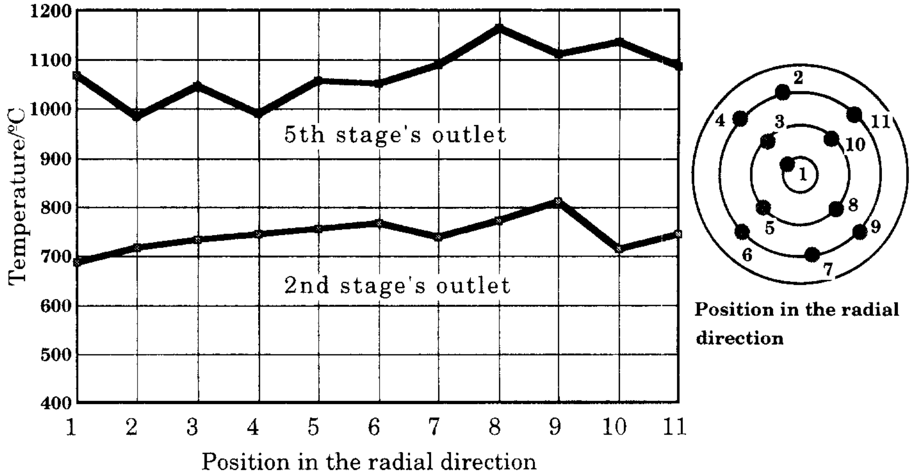


Fig. 9. Outlet temperature distribution of the second- and sixth-stage catalysts.

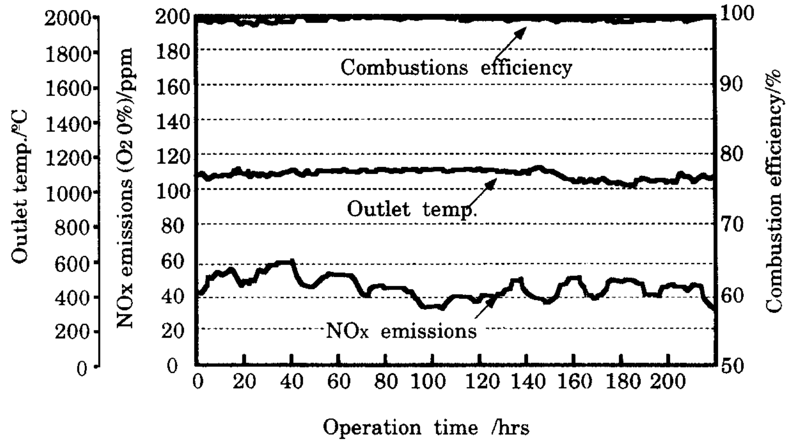


Fig. 10. Results of a continuous 215-hour continuous operation test of the catalytic combustor turbine.

ciency, and pressure loss ratio were almost attained. Fig. 9 shows the outlet temperature distribution of the second- and fifth-stage catalysts in the steady state. The temperatures in the second- and fifth-stage catalysts vary below their allowable temperatures with long term durability. These variations seem to be due to the variations of the catalyst inlet temperatures which were shown to be about 50°C in a measurement at four points, and those of the catalyst inlet fuel–air ratio. It can be seen that all the catalysts worked well since the temperature distributions in the catalysts were small and the temperature increase profile from the second- to the fifth-stage catalysts agree fairly well with that of Fig. 4.

5.3. A 215-hour continuous operation test

Fig. 10 shows the results of a continuous 215-hour operation test under the rated load. A combustion efficiency higher than 99% and catalyst outlet temperatures of about 1100°C were maintained throughout the test, while NO_x emissions varied from 60 to 35 ppm. The variations of NO_x emissions are due to the fact that we controlled not the air bypass valve but only the preheating fuel flow to keep the combustion efficiency high against the variations of the engine performance caused by the ambient temperature changes in order to avoid faulty operation especially during the night. Table 5 shows the catalytic combustor performance after a 215-hour continuous opera-

Table 5
Catalytic combustor performance after 215-hour continuous operation

Conditions		Results	
Turbine load	165.4 kW	Mean catalyst outlet temp.	1080°C
Compressor inlet air temp.	19.7°C	Exhaust gas composition	
Combustor inlet air temp.	364°C	Total hydrocarbons	17 ppm
Combustor inlet pressure	8.36 atm	Carbon monoxide	265 ppm
Mean catalyst inlet temp.	452°C	NO_x	8.2 ppm
Preheating fuel flow rate	12.3 Nm^3/h	Carbon dioxide	2.657%
Main fuel flow rate	89.5 Nm^3/h	Oxygen	16.21%
		Combustion efficiency	35.9%
		Pressure loss ratio	4.02%

tion. The target values for NO_x emissions, combustion efficiency, and pressure loss ratio were all attained.

Inspection of the catalysts and their holder after the test confirmed that no physical damage had occurred.

5.4. Sudden-stop tests of the engine

Sudden-stop tests of the engine at the rated load were carried out by using a newly set catalyst system in order to demonstrate the crack durability of the catalyst system. The procedure from the engine start-up to the rated load operation was like that described in 5.1 and 5.2. After one hour operation at the rated load, the fuel flow was suddenly stopped and the engine load was removed at the same time. The similar tests from the engine start-up were repeated four more times with at least two hours-cooling intervals.

Inspection of the catalysts and their holder after the tests also confirmed that no physical damage had occurred.

6. Conclusion

The possibility of a new combustion catalyst system for gas turbines composed of ceramic honeycomb catalysts directly formed by using manganese-substituted hexaaluminate and noble metal-carrying cordierite honeycomb catalysts has been demonstrated in a 160 kW prototype catalytic combustor turbine test.

As the next step, the conceptual design and feasibility study of the catalytic combustors for 1000 to 1500 kW-class gas turbines, investigation of combustion control techniques to cope with sudden load changes, and estimation of the catalyst life of at least one year, etc. will be required.

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