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Catalysis Today 26 (1995) 345–350

CATALYSIS TODAY

Development of a hybrid catalytic combustor for a 1300°C class gas turbine

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Abstract

The hybrid catalytic combustor concept proposed by the authors has an advantage concerned with catalyst durability, because the catalyst is maintained below 1000°C even for application to 1300°C class gas turbines. A full-scale hybrid catalytic combustor has been designed for a 200 MW (1300°C) class gas turbine. The catalyst bed was 450 mm in diameter and consisted of a Pd/alumina washcoat on a cordierite monolith. In experiments, the combustor has demonstrated the capability of meeting the NO_x emission level of SCR (selected catalytic reduction) during atmospheric pressure testing. To predict the catalyst performance at an elevated pressure, the characteristics of the catalyst were studied using a small scale reactor test, and a material property test using a DTA/TGA–Q.MASS system. The catalyst showed a higher activity in the oxidized state (PdO) than in the metallic state (Pd). This activity difference was governed by the equilibrium of the oxygen release from PdO in bulk. It was considered that oxidation rate of the metallic Pd in bulk was not so high and this caused self-oscillation for the Pd catalyst around the temperature of the oxygen release equilibrium. Even below the temperature of the oxygen release equilibrium, both surface and bulk (lattice) oxygen of the PdO was consumed by the methane oxidation reaction, and resulted in a lack of surface oxygen on the catalyst. This caused a reversible decrease in the catalyst activity during combustion testing, and indicated that the oxygen dissociation step was a rate limiting step in the catalytic combustion.

Keywords: NO_x; Combustor; Gas turbine; Hybrid catalytic combustor

1. Introduction

Large scale combined cycle power stations, consisting of gas turbines and steam turbines, have been in commercial operation for the last decade in Japan. These power stations have been equipped with a unit, which combines steam injection into a combustor and a selective catalytic reduction (SCR) system, for reducing NO_x produced in the gas turbine combustor. SCR permits very low NO_x emission but imposes attendant cost and performance penalties.

Catalytic combustion is an alternative technology under development that has the potential of meeting the SCR emission level and cost reduction [1]. However, further development efforts are needed to make a catalytic combustor commercially available. One of main problems in developing a catalytic combustor is the durability of the catalyst at high temperature operation. The catalyst bed should withstand temperatures above

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SSDI 0920-5861(95)00157-3

1300°C for current and next generation gas turbines for the existing catalytic combustor concept but no catalyst has been successfully developed to meet this requirement.

A hybrid catalytic combustor concept proposed by the authors has an advantage concerned with catalyst durability because the catalyst is operated below 1000°C, utilizing the gas phase combustion occurring downstream of the catalyst bed [2,3]. The hybrid catalytic combustor concept had been studied by the authors using small scale reactors (30 mm and 100 mm diameter catalysts) at pressurized conditions (0.1–0.6 MPa) [4,5].

These studies indicated that NO_x emissions did not depend on pressure and ranged below 10 ppm. This paper summarizes the atmospheric pressure test result of a full-scale hybrid catalytic combustor designed for a 200 MW (1300°C) class gas turbine and reports the characteristics of the catalyst that have been studied by a small scale reactor test and a material property test.

2. Full-scale combustor testing

2.1. Combustor design

Fig. 1 shows the conceptual model of the hybrid catalytic combustor for gas turbines. The combustor consists of a precombustion zone (Z1), a premixing zone (Z2), a catalyst zone (Z3) and a gas phase combustion zone (Z4) equipped with a bypass valve. Fuel is divided into three parts. Each fuel flow rate is controlled according to the gas turbine load. The precombustion zone maintains the catalyst inlet gas temperature by firing fuel (F1) to initiate the catalytic reaction. Fuel (F2) is premixed with air in the premixing zone and burns catalytically in the catalyst zone. The catalyst bed temperature is maintained below 1000°C by designing both the catalyst and the operation conditions including inlet gas velocity, catalyst inlet gas temperature, and fuel/air ratio. The hot catalyst exhaust, containing unburnt fuel, mixes with the additive fuel (F3) and burns completely in the gas phase combustion zone without any catalyst. The firing temperature of the gas phase combustion zone was designed to be around 1500°C and employed a multi-nozzle construction to enhance both flame stability and fuel mixing. The turbine inlet temperature is controlled by injecting dilution air through the bypass valve according to the gas turbine load.

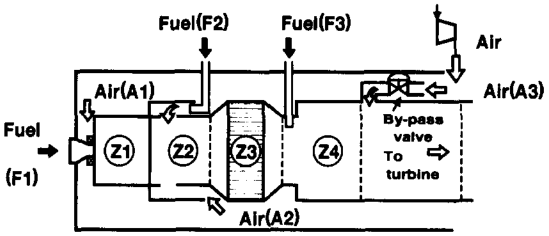

Fig. 1. Conceptual model of a hybrid catalytic combustor.

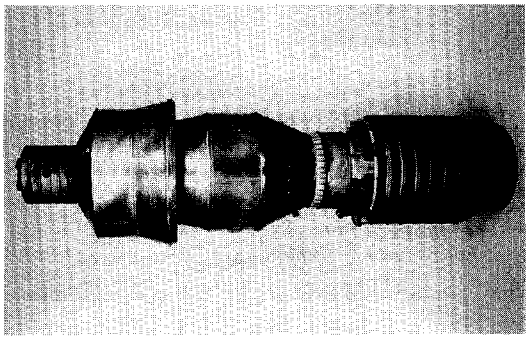

Fig. 2. Assembly of full scale combustor.

Fig. 3. Approach view of catalyst bed.

A full-scale combustor has been developed [6], based on the above concept, as shown in Fig. 2, which is equivalent to one set of combustors used in a 200 MW class gas turbine. Fig. 3 shows an approach view of the catalyst bed. The catalyst bed was 450 mm in diameter and consisted of a Pd/alumina washcoat on a cordierite monolith.

2.2. Atmospheric pressure test result

A combustion test of the full scale combustor was carried out at atmospheric pressure with a

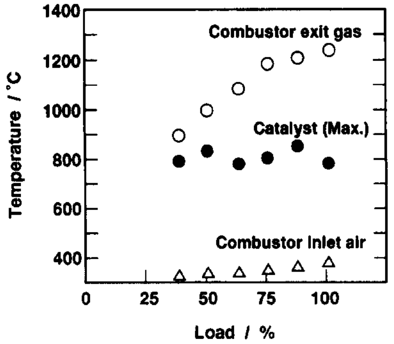

Fig. 4. Result of temperature measurement.

natural gas fuel. The test conditions were simulated to the operating conditions for a 1300°C class gas turbine except for the pressure.

Fig. 4 shows the experimental result of temperature measurement for inlet air, catalyst and exit gas during the combustion test. The horizontal axis represents operation conditions corresponding to a gas turbine load. This result demonstrates the typical characteristics of this hybrid catalytic combustor concept, showing the catalyst temperature to be around 800°C in spite of the 1300°C class gas turbine firing temperature.

The measured emission characteristics are shown in Fig. 5. The CO emission level was rather high, ranging from 100 ppm to 200 ppm, but will be improved by modifying the combustor design criteria, such as the firing temperature of the gas phase combustion zone. NO_x emission was below 3 ppm, which was generated in the precombustion zone and the gas phase combustion zone. This low NO_x performance suggests that well-mixed lean combustion occurred in the gas phase combustion zone without a local hot region and that NO_x formation was small in the precombustion zone because of its low temperature rise. It is thought that these emission characteristics were achieved by a combination of the catalyst zone and the gas phase combustion zone.

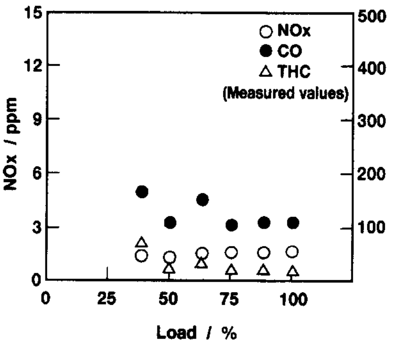

Fig. 5. Emission characteristics.

3. Catalyst characteristics

It is well-known that noble metal catalysts show a high activity for the oxidation of hydrocarbons. However, they have not been able to be applied to conventional catalytic combustion because they tend to volatilize at high temperature and in the oxidizing atmosphere in gas turbine combustors. The hybrid catalytic combustor concept, because of its low operating temperature, provides the possibility of applying noble metal catalysts to a gas turbine combustor.

Pd is one of the candidate catalysts for firing natural gas because of its low ignition temperature. However, it has already been mentioned concerning this work that the activity of a Pd catalyst decreases and oscillates by itself above 750–800°C during atmospheric pressure combustion testing [7]. The authors consider that this phenomenon is due to oxygen release from PdO in bulk which also occurs at the same temperature range.

Fig. 6 and 7 show one set result of DTA/TGA–Q.MASS (Quadrupole mass spectrometer) on a Pd catalyst powder. The Pd catalyst powder consisted of palladium and stabilized zirconia (YSZ). The initial state of palladium was checked to be metallic, prior to use in testing. Oxidation of palladium started at around 400°C, showing an

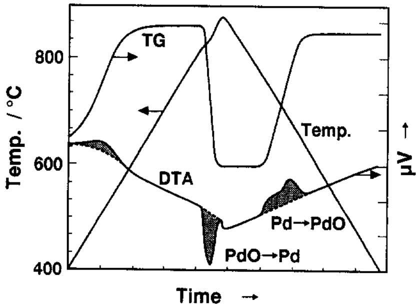

Fig. 6. DTA/TGA of Pd-catalyst (O_2/N_2).

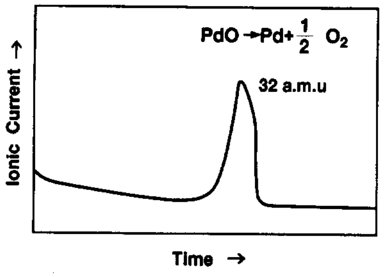

Fig. 7. TPD of Pd-catalyst (Q-MASS).

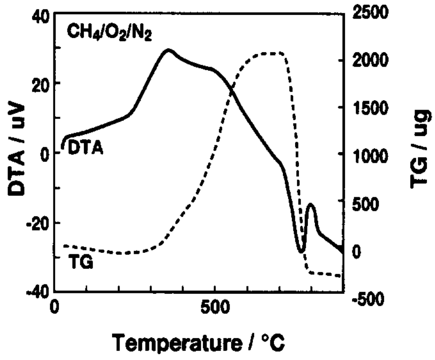

Fig. 8. DTA/TGA of Pd-catalyst ($CH_4/O_2/N_2$).

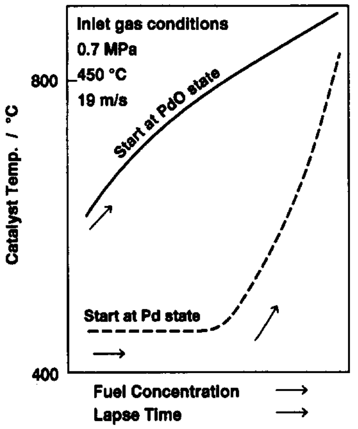

Fig. 9. Activity difference between PdO and Pd.

Table 1
Typical composition of fuel

Composition	vol.-%
CH_4	90.8
C_2H_6	2.0
C_3H_8	1.9
C_4H_{10}	4.8
CO_2	0.2
H_2	0.3
LHV, MJ/Kg	48.9

increase in TG and a broad peak of DTA (exothermic reaction), shown in Fig. 6. This oxidation was verified to be the oxidation of the palladium in bulk because the amount of the TG increase corresponded to the theoretical weight increase in formation of PdO. Above 780°C a decrease in TG and an endothermic DTA peak accompanied by oxygen release from PdO, as shown in Fig. 7, was observed. The palladium was oxidized again during the cooling step. These figures confirmed that a reversible change between PdO and Pd occurs at almost the same temperature as the beginning of self-oscillation and activity decrease.

A similar analysis was carried out under a flowing methane (0.5%), oxygen (5%), and nitrogen mixture. The result is shown in Fig. 8. A DTA peak around 350°C corresponds to oxidation of palladium and a DTA peak around 500°C corresponds to oxidation of methane on the catalyst. It was proved by TG and Q. MASS analyses that the palladium oxidation and the methane oxidation started simultaneously at around 300°C. These results indicate that oxidation of palladium is necessary to initiate the methane oxidation reaction. A decrease in TG accompanied by an endothermic DTA peak at 700°C results from the equilibrium of oxygen release of PdO in bulk, which was not affected by the methane oxidation reaction. This released oxygen was observed as an oxygen molecule by Q.MASS.

Fig. 9 shows an example of the activity difference between the oxidized state (PdO) catalyst and the metallic state (Pd) catalyst during combustion testing at 0.7 MPa. The test was performed on a 30 mm diameter honeycomb catalyst by increasing the fuel concentration with the lapse of time. The inlet gas temperature was controlled at 450°C by electric furnace. Desulphurized town gas was used as the fuel. Typical composition of the town gas used in the testing is shown in Table 1. The oxidized state (PdO) catalyst was prepared by calcination in air, while the metallic state (Pd) catalyst was prepared by rapid cooling of the catalyst from a temperature above the oxygen release equilibrium temperature. The states of these catalysts were certified by XRD (X-ray dif-

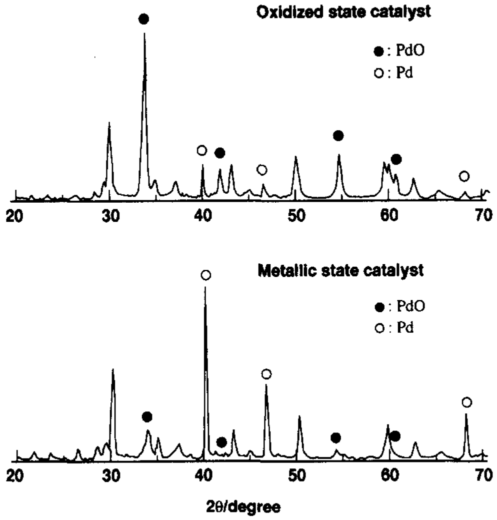

Fig. 10. XRD patterns of prepared catalysts.

fraction) prior to the combustion testing. The result is shown in Fig. 10. The figure shows that the dominant peaks were PdO and Pd respectively. Fig. 9 indicates that the activity of the metallic state catalyst is much lower than that of the oxidized state catalyst at the beginning of the test and that activity increases with increasing fuel and duration. This suggests that the metallic state catalyst is oxidized under the reaction condition and that the oxidation rate of the metallic Pd in bulk is not high enough, at this inlet gas temperature, to recover its activity immediately. It is also considered that this low oxidation rate of the metallic Pd in bulk causes self-oscillation between PdO and Pd around the equilibrium temperature. This is because the catalyst temperature is maintained at a constant value around the oxygen release equilibrium temperature when there is sufficient fuel if the palladium states immediately reach a steady state determined by the oxygen release equilibrium.

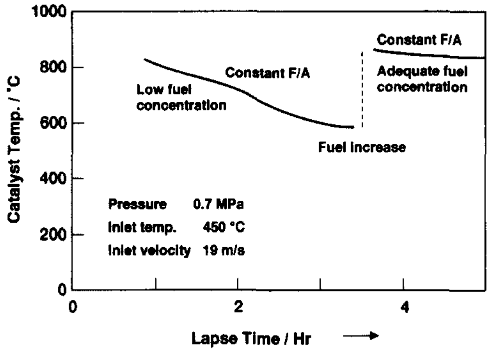

Fig. 11. Activity stability during combustion testing.

Fig. 11 shows the stability of the activity during the 30 mm diameter catalyst combustion testing at 0.7 MPa. The activity change was small in case of adequate fuel concentration, while the activity decreased with the lapse of time for low fuel concentration. This activity decrease was identified as a reversible activity change by repeating the combustion testing. After the combustion testing, the catalyst was analyzed by XRD to investigate this activity decrease. The XRD result are shown in Fig. 12. The figure indicates that palladium state of the catalyst was changed from the oxidized state (PdO) to the metallic state (Pd). This XRD result was not predicted considering the oxygen partial pressure and the catalyst temperature during this combustion testing, because the palladium state was expected to be the oxidized state in view of the oxygen release equilibrium at these testing conditions. These suggest that both surface and lattice oxygen of the PdO was consumed by the methane oxidation reaction during the combustion testing and that the activity decrease resulted from lack of surface oxygen. The 0.1 MPa and 0.4 MPa tests were also carried out using the 30 mm diameter catalyst. The result indicated that the reversible activity decrease was accelerated by the pressure.

The reversible activity decrease might be caused by the unbalancing of reaction rate

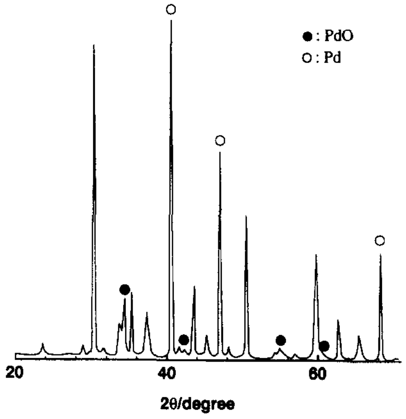

Fig. 12. XRD pattern of catalyst after combustion testing.

between the oxygen dissociation ($O2 \rightarrow O_{ad}$) step and the following steps on the catalyst surface. It is considered that the oxygen dissociation step is the rate limiting step in this catalytic combustion system.

4. Conclusion

A hybrid catalytic combustor has been designed for a 200 MW (1300°C) class gas turbine. The combustor demonstrated an ultra-low NO_x capability during atmospheric pressure testing experiments. The catalyst showed a higher activity in the oxidized state (PdO) than in the metallic state (Pd) in bulk. This activity difference is determined by the oxygen release equilibrium from PdO in bulk. Even though the palladium state in bulk should be the oxidized state in view of the oxygen release equilibrium, the oxidized state is changed into the metallic state by consumption of lattice oxygen for methane oxidation. This causes a reversible decrease in the catalyst activity at combustion testing.

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