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High-pressure reaction and emissions characteristics of catalytic reactors for gas turbine combustors

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Abstract

The reaction and emissions characteristics of catalytic reactors comprising noble metal catalysts were investigated using homogeneous mixtures of natural gas and vitiated air at pressures up to 2.9 MPa. The mixture temperatures at inlet ranged from 500 to 700°C and the fuel–air ratio was increased till the exit gas temperature reached about 1200°C. Values of combustion efficiency greater than 99.5% and nitrogen oxides emissions for all catalytic reactors tested were less than 0.2 g NO_2/kg fuel (2 ppm (15% O_2)) for all reactors at reactor exit gas temperatures higher than about 1100°C. Combustion efficiency decreased with increasing pressure in the heterogeneous-reaction controlled region, though a pressure increase favored homogeneous, gas-phase reactions. Appreciable reactivity deterioration by aging for 1000 h at 1000°C was observed at lower mixture temperatures. A two-stage combustor comprising a conventional flame combustion stage and a catalytic stage was fabricated and its NO_x emissions and performance were evaluated at conditions typical of stationary gas turbine combustor operations. About 80% reduction in NO_x emissions levels compared with flame combustion was attained at 1 MPa pressure and 1180°C exit gas temperature, together with complete hydrocarbon combustion.

Keywords: Combustion; Reactors; Noble metals

1. Introduction

Nitrogen oxides (NO_x) emissions from stationary gas turbines for power and co-generation are regulated in the United States, Japan, and some European countries. It is very probable that more stringent regulations will be enforced in the near future. NO_x emissions increase steeply with combustion temperature and moderately with pressure and consequently the NO_x emissions from high-pressure, high temperature gas turbines, which are being developed for higher thermal efficiency, will increase. To meet the expected emission standards, the development of low-NO_x combustion technology for the advanced gas turbines is a major concern to gas turbine manufacturers. One of the candidates is catalytic combustion: earlier experimental studies using No. 2 oil [1–4], low-Btu coal gas [1,2,5], JP-4 fuel [6], and propane [7] demonstrated the potential of attaining ultra-low NO_x emissions at moderate pressures.

Since natural gas used in Japan contains neither sulphur nor nitrogen compounds that would lead to high-levels of NO_x and SO_x emissions, it is the primary fuel for gas turbines installed in urban and suburban areas. Previous studies [8,9] on the reactivity of catalysts for hydrocarbons show that methane is more difficult to oxidize on catalysts

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than the higher hydrocarbons. Additionally, the results of Ref. [1] shows that natural gas, of which major constituent is methane, requires higher mixture temperatures for attaining complete combustion than low-Btu coal gas and No. 2 oil. Hydrocarbon fragments from No. 2 oil, and CO and hydrogen in coal gas can be oxidized on catalysts at lower temperatures. The reaction characteristics of natural gas have been less intensively investigated, especially at pressures typical of gas turbine operations.

In the first phase of the present study, the reaction characteristics of four catalytic reactors, comprising noble metal catalysts, were investigated at elevated pressures up to 2.9 MPa using homogeneous mixtures of natural gas and vitiated air. In the second phase, a two-stage catalytic combustor, comprising flame combustion and catalytic combustion stages, was fabricated. The emissions and performance of the combustor were tested at conditions typical of combustors for stationary gas turbines.

Most of the natural gases imported to Japan contains a few percent of ethane and propane which can be oxidized on catalysts at lower temperatures than methane. A previous study [10] actually showed that the mixture temperature required for complete combustion in a catalytic reactor was lower for natural gas than for pure methane. The natural gas used in the present study was composed of 98.5–98.9% methane and 0.5–0.9% non-combustible constituents (air, carbon dioxide and water).

2. Experimental apparatus and procedures

Fig. 1 shows the details of the catalytic reactor test rig installed in a high-pressure combustion test facility at National Aerospace Laboratory. A compressor system of a pressure ratio of 50 was used to supply air to the test section. In the present experiments the air temperature was kept at a temperature of 400°C (the maximum allowable temperature for the air source) and the pressure was varied up to 2.9 MPa. The fuel–air ratio, defined as the ratio of mass flow rates of fuel and air, was varied up to a value where the calculated adiabatic gas temperature was close to the temperature limitation of the combustion test facility (1250°C). Preliminary tests showed that at 400°C all catalytic reactors failed to attain very high combustion efficiencies for the fuel–air ratios tested. So, a natural gas-fueled preburner of conventional configuration was used to preheat directly the mixtures to temperatures ranging from 500 to 700°C. A multi-venturi fuel injector composed of seven air passage, of which cross sectional view is schematically shown in Fig. 2, was used to inject the fuel into the vitiated air from the preburner. Four fuel orifices were drilled at the throat section on the wall of each venturi. A vane-type mixer and a honeycomb flow straightener were installed upstream of the catalytic reactor to provide uniform distributions of temperature, velocity and composition across the reactor inlet face.

The catalytic reactors contained three monolithic catalyst elements of 100 mm in diameter and 25 mm in length. Each element was supported by

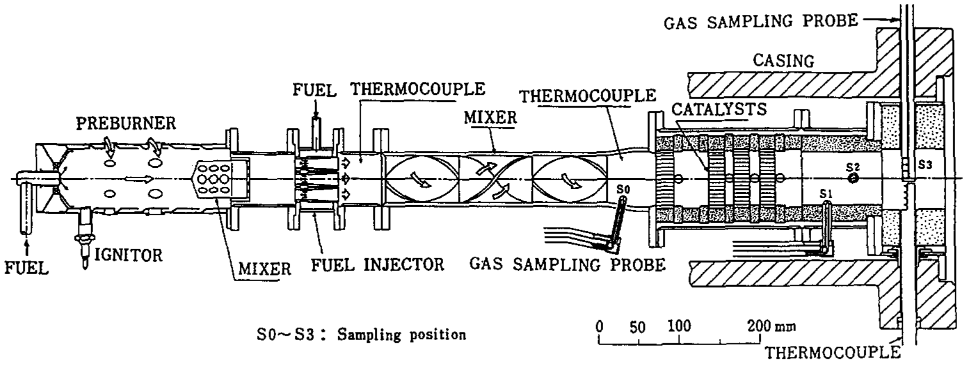

Fig. 1. Schematic drawing of high-pressure catalytic reactor test rig.

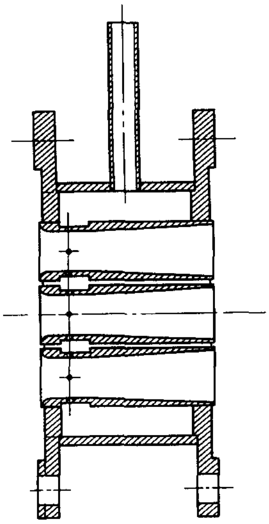

Fig. 2. Design of multi-venturi fuel injector.

Table 1
Combinations of catalysts in catalytic reactors tested

Catalytic reactor	1st and 2nd elements	3rd element
SKY A-A	SKY-A, Pd (100)	SKY-A, Pd (100)
SKY B-C	SKY-B, Pd/Pt (200)	SKY-C, Pt (100)
SKY B-C aged	SKY-B[a], Pd/Pt (200)	SKY-C[a] Pt (100)
SKY B3-D	SKY-B3, Pd/Pt(200)	SKY-D, Pt (100)

Numerical values in parentheses are cell density (cpsi).
[a] Aged for 1000 h at 1000°C.

four ceramic supporting rods, 10 mm in diameter, so that mixture was allowed to flow through the annular gap between the elements and the reactor casing wall. This led to more uniform temperature distributions across the catalyst inlet face and reduced thermal stresses in the elements.

The combinations of the catalyst elements in the reactors tested are summarized in Table 1. The element SKY-A is palladium, SKY-B and SKY-B3 are palladium/platinum (1:1), and SKY-C and-D are platinum catalysts. The monolith of SKY-A, SKY-B and SKY-C was cordierite and that of SKY-D was mullite. The symbol * represents the catalysts aged for 1000 hours at a temperature of 1000°C. The cell densities of the catalyst elements are shown in terms of cpsi (cells per square inches) in the parentheses. In contrast with the graded cell concept [11], elements with small cells were placed at the front of the reactor to increase heat release there. Complete oxidation of fuel in the catalysts was not intended and the gas-phase reaction downstream of the catalyst was utilized instead for complete oxidation of unreacted fuel and CO.

Experiments were made at inlet mixture temperatures of 500, 600 and 700°C, pressures of 0.98, 2.0 and 2.9 MPa, and at reactor reference velocities of 12 and 20 m/s. The reference velocity was defined as the vitiated air velocity averaged over the cross-sectional area of the catalytic reactor at the actual temperature and pressure. The reactor exit gas temperature was varied up to about

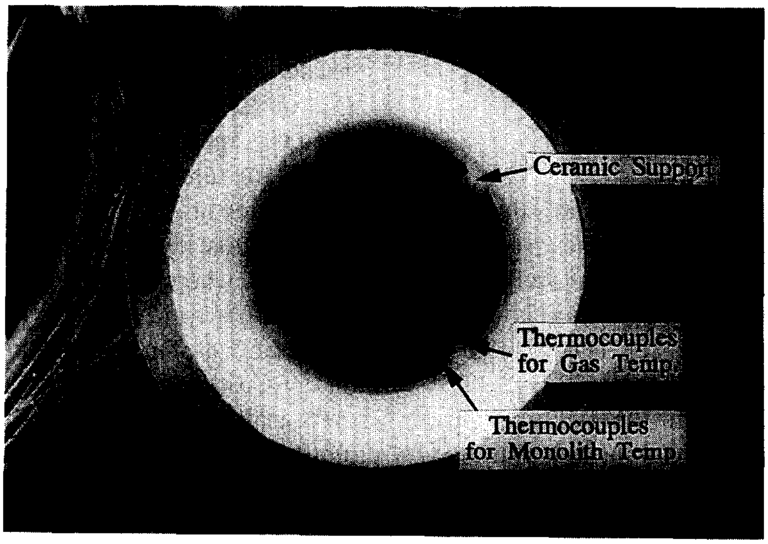

Fig. 3. Thermocouple settings for monolith and gas temperatures measurements.

1200°C. For the measurements of gas compositions, gas was sampled using water-cooled gas sampling probes placed at 70, 105 and 171 mm downstream of the outlet face of the third element, the sampling positions being shown in Fig. 1 by the symbols S1, S2 and S3. For monitoring the composition of the vitiated air during tests, gas was sampled with a water-cooled single-hole probe located just upstream of the reactor inlet (position SO in Fig. 1). Concentrations of NO, NO_2, CO, CO_2, O_2, and total hydrocarbons (HC) were determined by the standard gas analysis procedures: chemiluminescence for NO, non-dispersive infrared absorption for CO and CO_2, flame ionization for HC, and paramagnetic analysis for O_2. The measured oxygen concentrations in the vitiated air ranged from 16.4 to 18.6% depending on the degree of preheat by the preburner.

Reference monolith wall temperatures and gas temperatures were measured by two thermocouples cemented on the monolith and by two thermocouples positioned 5 mm downstream of each element, respectively, as shown in Fig. 3. The thermocouple junctions for the measurements of monolith temperature were inserted into channels to a depth of about 5 mm from the downstream end of a monolith and the ends of the channels were completely blocked with ceramic filler to prevent mixture from flowing the channels.

3. Experimental results

3.1. NO_x emissions

The emission indices for NO_x at conditions where high combustion efficiencies (typically greater than 99.5%) were achieved are summarized in Table 2, together with monolith temperatures of the third element, *T*c3, and the exit gas temperatures measured at position S3, *T*g,s3.

The NO_x emissions from the preburner were evaluated for gases sampled at the exit of the catalytic reactors (position S3) before fueling the catalytic reactor and those from the preburner and the catalytic reactor were measured at the same axial position after fueling the catalytic reactor. The amount of NO_x formed in the catalytic reactor alone was estimated based on the difference between the emissions levels measured before and after fueling the catalytic reactor. The difference was an order of magnitude smaller than the actually measured NO_x emissions levels and, as a results, the accuracy of the values for NO_x emissions levels for the catalytic reactors listed in Table 2 was limited by the subtracted error. It is also noted that neither absorption of NO_x from the preburner was detected for the catalysts in the limits of measurements accuracy. Nitrogen oxides emissions for all catalytic reactors tested were less than 0.2 g NO_2/kg fuel (2 ppm (15% O_2)) for most of the test conditions while the nitrogen oxides emissions for the preburner varied from 5.9 g NO_2/kg at 500°C inlet mixture temperature and 0.98 MPa to 9.3 g NO_2/kg at 700°C and 2.9 MPa.

The measured monolith temperatures of the third element were close to the exit gas temperature when complete combustion was attained. High combustion efficiency was not obtained with fuel-lean mixtures of which theoretical combustion temperature was lower than about 1000°C for all combinations of catalysts.

3.2. Combustion efficiency

The combustion efficiencies measured for all reactors at position S1 are compared in Fig. 4. Reactor SKY B-C was found to be the most reactive. The aged SKY B-C, being least reactive at 600°C mixture temperature, achieved complete combustion at 700°C mixture temperature. It was more reactive than the SKY B3-D at smaller fuel–air ratios, where heterogeneous reaction was the major exothermic reaction.

The effects of mixture temperature and pressure on combustion are shown typically in Fig. 5 for the SKY B-C, where combustion efficiencies were plotted as a function of adiabatic combustion temperature calculated based on the stoichiometry and initial temperature of the mixtures. With increasing fuel–air ratio (moving along the abscissa to

Table 2
Emissions for NO_x at conditions for attaining high combustion efficiencies

p (MPa)	Tin (°C)	F/A (10^{-2})	EI (NO_x)[a] (g NO_2/kg)	Reactor fuel	*η* (%)	*T*g,S3 (°C)	*T*c3 (°C)
0.98	500	1.66	0.2±0.1	SKY B-C	99.7	1016	1102, 1123
	600	1.53	<0.1	SKY B-C	99.7	1181	1187, 1162
		1.73	<0.2	SKY B3-D	99.6	1223	1221, 1214
	700	1.35	<0.2	SKY B-C aged	99.8	1181	1170, 1178
2.0	600	1.62	0.6±0.3	SKY B-C	99.9	1197	1150, 1164
		1.72	<0.2	SKY B3-D	99.7	1230	1127, 1128
	700	1.41	<0.2	SKY B3-D	99.8	1205	1186, 1180
		1.32	<0.2	SKY A-A	99.9	1176	1180, 1185
		1.24	0.2±0.1	SKY B-C aged	98.1	1182	1084, 1103
2.9	700	1.33	0.3±0.2	SKY B3-D	99.9	1209	1204, 1202
		1.32	<0.2	SKY A-A	100	1086	1086, 1091

[a] 1 EI (NO_x) = 9.73 ppm (15% O_2).

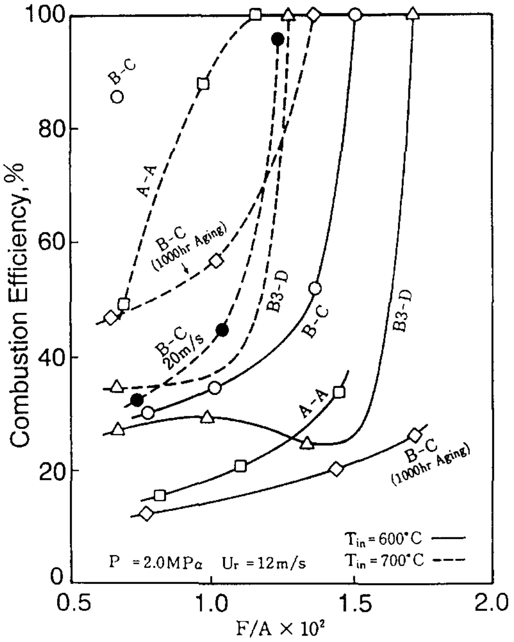

Fig. 4. Comparison of combustion efficiencies of all reactors at 12 m/s reference mixture velocity and 2 MPa pressure. For SKY B-C data measured at 20 m/s are also presented.

the right in Fig. 5), combustion efficiency was generally decreased at first and then increased. In the region where combustion efficiency is decreasing, reaction occurs only on the catalyst surface and limited amount of fuel was oxidized. The increase in combustion efficiency brought by an increase in fuel–air ratio is due to the initiation of homogeneous reaction in the gas-phase in the monolith, is catalytic combustion. The effect of pressure on combustion varied depending on mixture temperature: combustion efficiency decreased with increasing pressure at mixture temperatures of 500°C and 600°C, as is shown in Fig. 5. The combustion efficiency data measured with other reactors showed that at 700°C mixture temperature combustion efficiency increased with pressure. At higher mixture temperatures, an increase in pressure leads to greater combustion efficiencies since homogeneous reaction in the gas-phase, which is promoted by a pressure increase, becomes predominant in the reactor. At lower mixture temperatures, heterogeneous surface reaction is a major exothermic reaction and therefore a large catalytic surface area is required

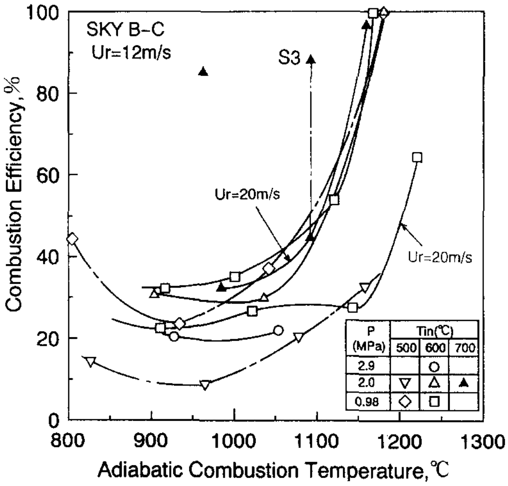

Fig. 5. Effects of operating conditions on combustion efficiency measured at position S1 except for a point noted as S3 measured at position S3.

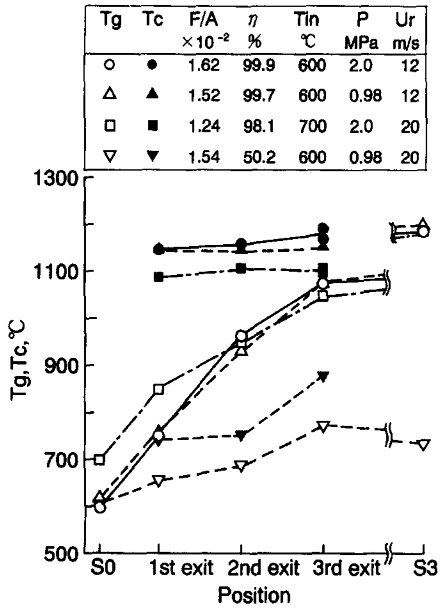

Fig. 6. Gas and monolith temperatures at exits of catalyst elements and positions S0 and S3.

for improving combustion efficiency at increased pressures. With increasing reference velocity, the fuel–air ratio required to achieve complete combustion shifted to a larger equivalence ratio, as shown by the data measured at 20 m/s.

Under some conditions, appreciable increases in combustion efficiency due to gas-phase, homogeneous reaction were measured downstream the catalysts, as reported in previous studies [12,13]. The result at 20 m/s reference velocity and 700°C mixture temperature is a typical example: the data point denoted as S3 shows that as much as 50% of the fuel reacted in the gas phase between positions S1 and S3 (100 mm in length). Combustion was incomplete in the reactor due to the short residence time, but the gas temperature at the reactor exit was high enough to sustain further reaction downstream the reactor.

3.3. Monolith and gas temperatures

The monolith temperature was found to be always higher than the gas temperature, due to the exothermic reaction on the monolith surface. In Fig. 6 are compared the monolith temperatures *T*c, and the gas temperatures, *T*g, measured for the reactor SKY B-C at the exit of each catalyst element. The gas temperatures measured at position S3 are also plotted in the figure. In the case of high combustion efficiency the monolith temperatures were close to the adiabatic combustion temperature even for the first element. However, the gas temperatures there were appreciably lower than the monolith temperature and the maximum temperature difference was 400°C. On the other hand, in the case of low combustion efficiency, the monolithic temperatures were less than 900°C and gas temperatures were around 700°C. Therefore, gas-phase reaction was not appreciable as the data in the figure shows: at gas temperatures lower than about 1100°C, homogeneous gas-phase reactions are not sufficiently active enough to achieve complete combustion.

To examine at what temperature the gas-phase reaction becomes appreciable, the gas temperature at the exit of the third catalyst element, *T*g3, and that at position S3, *T*g,s3, are cross-plotted in Fig. 7. It is seen from the figure that at *T*g3 above 800°C, the gas-phase reaction is sustained downstream of the catalytic reactor, and that at *T*g3 higher than 900°C, the exit gas temperature nearly reached the adiabatic combustion temperature.

In a previous atmospheric experiments on the reaction of lean propane–air mixtures injected into vitiated high-temperature gas streams, it was

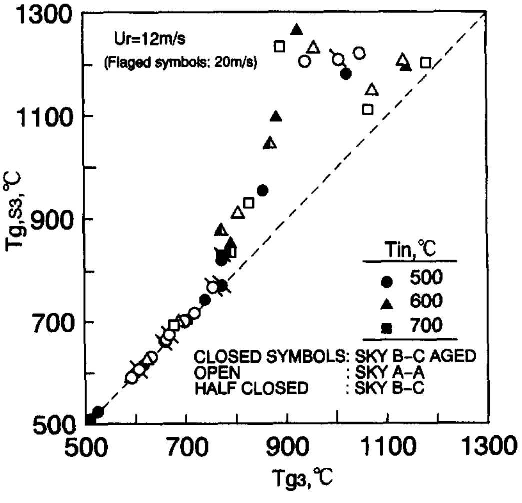

Fig. 7. Correlation between gas temperatures measured at positions S1 and S3.

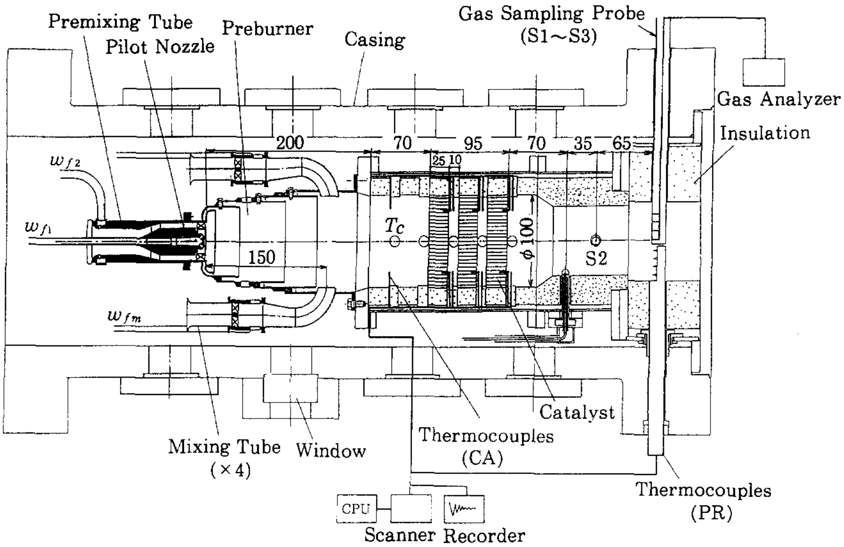

Fig. 8. Schematic drawing of catalytic gas turbine combustor tested.

shown that the gas-phase reaction initiated at about 900°C [14]. The comparison of the temperatures for gas-phase reaction suggests that the gas-phase reaction occurs at lower temperatures at elevated pressures than at atmospheric pressure.

4. Emission and combustion characteristics of a catalytic combustor

A two-stage model combustor, schematically shown in Fig. 8, was fabricated and its performance was evaluated at simulated gas turbine combustor operating conditions. The details of the combustor were described in a previous publication [15]. The first stage is a conventional swirl-stabilized diffusion flame combustor and the second stage is a catalytic reactor. Catalytic reactor configurations shown in Table 1, except for the aged, were tested. Lean premixed air and natural gas was injected from the mixing tubes and mixed with the burned gas from the first stage before entering the catalytic stage. The profiles of fuel/air ratio and gas temperatures at the inlet of the catalytic reactor were measured in preliminary atmospheric combustion tests. They were very consistent with each other and the measured fuel–air ratios and gas temperatures were within 10% and 25% of the area-averaged values, respectively.

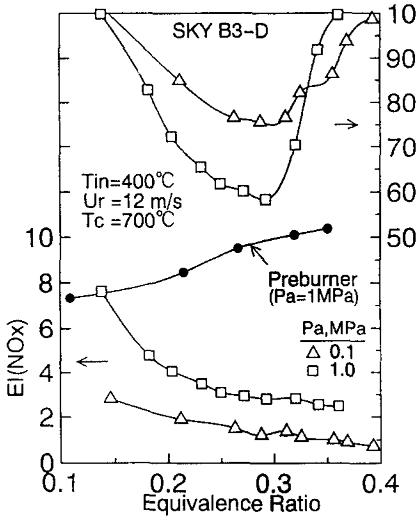

Fig. 9. Combustion efficiencies and NO_x emissions levels of a catalytic gas turbine combustor compared with those of a conventional preburner.

The tends of combustion efficiency and NO_x emissions with overall equivalence ratio measured for reactors with non-aged catalysts were similar. Fig. 9 typically shows the combustion efficiency and nitrogen oxides emissions levels of the combustor fitted with the SKY B3-D reactor measured at pressures of 0.1 and 1.0 MPa. The combustion efficiency of the preburner was very close to 100%. With increasing fuel supply to the catalytic stage the combustion efficiency decreased towards a minimum and then increases steeply to

100%. The steep increase was due to high heat release rate by the gas-phase reaction. The equivalence ratios required to attain complete combustion shifted to the leaner side with increasing pressure. The comparison of the results at 1.0 and 0.1 MPa clearly shows that gas-phase reaction was promoted at increased pressures. In the heterogeneous reaction region, however, the combustion efficiency at 0.1 MPa is lower than that at 1.0 MPa.

The amount of NO_x emissions was, therefore, primarily determined by the NO_x formation in the flame combustor. The emission indices for NO_x measured in the conventional flame combustion mode are also plotted in the figure for comparison. About 80% reduction of NO_x emissions was achieved at complete combustion conditions. It is postulated that a further reduction should be attainable if the diffusion flame preburner is replaced by a low-NO_x lean-premixed burner. Fragmented hydrocarbons and CO that would be produced by very lean operation of the lean-premixed preburner may favor the catalytic reaction, as previously reported [16]. The pressure loss of the combustor was as small as 1.2% at a combustor reference velocity of 10 m/s and at a pressure of 2 MPa. Combustion efficiency at smaller equivalence ratios and lower inlet temperatures could be improved without excessive increase in pressure loss by adding another element to the catalytic stage.

5. Conclusions

Reaction characteristics of catalytic reactors comprising noble metal catalysts for natural gas were experimentally investigated at pressures up to 2.9 MPa and inlet mixture temperatures ranging from 500°C to 700°C, being followed by NO_x emissions and performance tests of a catalytic combustor with a conventional diffusion flame preburner. Major results are summarized as follows:

(1) Very high combustion efficiency was attained at conditions where the outlet gas temperature was higher than about 1100°C because of gas-phase, homogeneous reaction. The reactions downstream of the catalytic reactor become appreciable at catalytic reactor exit gas temperatures above 800°C, and complete combustion is obtained at gas temperatures above 900°C.

(2) The fuel–air ratio required to achieve complete combustion increases appreciably with increasing mixture velocities and for aged catalysts. Even the aged catalysts showed high reactivity at 700°C mixture temperature.

(3) With increasing pressure, combustion efficiency increased in the homogeneous reaction controlled region, while decreased in the heterogeneous reaction region.

(4) The monolith temperature was higher than the gas temperature, with the temperature difference being as large as 400°C for the first catalytic element.

(5) The amount of nitrogen oxides emissions for the catalytic reactors were generally smaller than 0.2 g NO_2/kg fuel at most of the test conditions.

(6) The emission index for the two-stage catalytic combustor at 1.0 MPa pressure and 1200°C outlet gas temperature was about 2 g NO_2/kg fuel, lower by 80% than that for the conventional flame combustor at 1.0 MPa.

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