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Catalysis Today 26 (1995) 329–335

CATALYSIS TODAY

Catalytic combustion technology to achieve ultra low NO_x emissions: Catalyst design and performance characteristics

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Abstract

A catalytic combustion system has been developed which feeds full fuel and air to the catalyst but avoids exposure of the catalyst to the high temperatures responsible for deactivation and thermal shock fracture of the supporting substrate. The combustion process is initiated by the catalyst and is completed by homogeneous combustion in the post catalyst region where the highest temperatures are obtained. Catalysts have been demonstrated that operate at inlet temperatures as low as 320°C at 11 atm total pressure and conditions typical of high performance industrial gas turbines. The ignition temperature is shown to correlate with the specific catalytic activity of the washcoat layer over a rather broad range of activities. A reaction model has been developed that can predict ignition behavior from the measured catalytic activity.

Keywords: Combustion; Nitrogen oxides; Catalytic combustion; Palladium; Gas turbine

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1. Introduction

In traditional catalyst systems applied to catalytic combustion, the fuel/air mixture, with a composition to achieve the required combustor outlet temperature when combusted adiabatically, is fed to the catalyst [1]. As the catalytic reaction occurs, the catalyst surface temperature rises rapidly until the catalyst surface reaction becomes diffusion limited and at this point the catalyst substrate temperature will be close to the adiabatic combustion temperature of the fuel/air mixture. This results in thermal sintering of the support surface area, thermal sintering and vaporization of active components such as noble metals and thermal shock fracturing of ceramic supports.

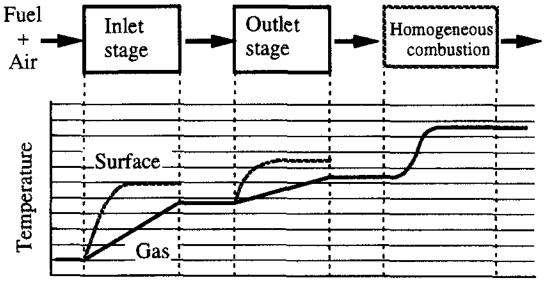

Fig. 1. Schematic diagram of low NO_x catalytic combustion system.

Recently, a novel approach to catalytic combustion was described that maintains the catalyst substrate at low temperatures through partial combustion of the fuel in the catalyst and completes the combustion down stream of the catalyst [2,3]. This approach is shown schematically in Fig. 1. The full fuel/air mixture to achieve the required

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SSDI 0920-5861(95)00155-7

combustor exit temperature is fed to the catalyst. Reaction on the catalyst results in a rise in the catalyst substrate temperature but the temperature rise is limited to a relatively low value. The gas temperature rises due to heat transfer from the hot catalyst substrate. Subsequent stages may be required with higher wall temperatures to achieve the required catalyst outlet gas temperatures. The partially combusted fuel air mixture then exits the catalyst and is combusted in a homogeneous gas phase reaction that causes the mixture to reach the full adiabatic combustion temperature. Several important aspects of the system design are:

1. *Inlet stage*
   - Designed to maintain a very low wall temperature
   - Low substrate temperature makes possible a stable, very high catalytic activity necessary for catalyst operation at the compressor discharge temperature
2. *Outlet stage*
   - Can be designed with a higher substrate temperature to provide the required catalyst outlet gas temperature
   - Lower catalyst activity is acceptable since a higher inlet gas temperature is provided by the inlet catalyst section
3. *Homogeneous combustion region*
   - Localizes the high temperature after the catalyst
   - Completes combustion of the fuel and burnout of CO and unburned hydrocarbons to the required levels necessary to meet emissions requirements
   - Produces the required combustor outlet temperature; this can be quite high, 1250 to 1450°C for modern high efficiency gas turbines.

Catalyst systems have been demonstrated at pressures from 10 to 20 atmospheres and combustor outlet temperatures from 1225°C to 1500°C [4]. Measured emissions were in the range of 0.2 ppm at 1225°C up to 2 ppm at 1500°C (at 15% O_2). This covers the range of most current and future gas turbine engines.

This approach, limiting the catalyst temperature substantially below the complete combustion temperature of the fuel/air mixture has a number of advantages. Wider range of substrate materials can be used including conventional ceramics and metals. The lower catalyst operating temperature can maintain higher catalytic activity and will have increased durability through decreased sintering. This approach extends catalytic combustion to substantially higher combustor discharge temperatures. With more traditional catalytic combustion in which the catalyst is at the combustor discharge temperature, extension to current and future high turbine inlet machines would require the development of new substrate ceramics, high surface area support materials and new catalysts that would be stable at these higher temperatures.

2. Experimental

2.1. High-pressure catalytic combustion test system

The results described in this paper were obtained in a high-pressure catalytic combustion test reactor located at Catalytica, Inc. and shown schematically in Fig. 2. This reactor uses a 50 mm (2.0 in) diameter catalyst and can be operated over a wide range of conditions that simulate the catalyst environment in current industrial gas turbines including pressures up to 20 atmospheres. The air is supplied by a conventional air compressor with facilities for removing oil and other contaminants from the compressor to supply

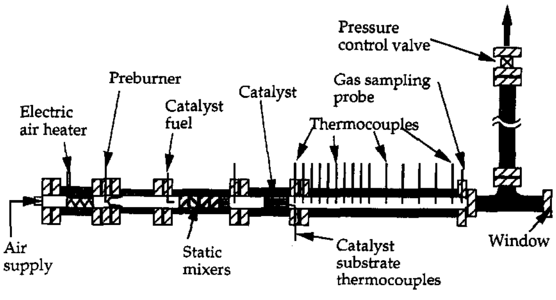

Fig. 2. High-pressure catalytic combustion reactor system.

reasonable clean air to the reactor system. The air is metered through several mass flow controller systems to cover the range from 1000 to 11 000 SLPM (standard liters per min). The air flows through a closed loop controlled 120 kW electric heater that can provide non-vitiated air at temperatures from 25 to 500°C. This gas flow then passes through a conventional diffusion flame burner that uses natural gas (methane) fuel to simulate the preburner in the gas turbine system. This flame combustor can raise the air temperature to ca. 800°C. Subsequently, the catalyst fuel is injected through a multiple port single tube and then mixed with the air using a blade type static mixer (Sulzer model SMV). The catalyst section is easily removable for changing the catalyst and numerous ports are present to introduce thermocouples for measurement of catalyst and gas temperatures in the catalyst as well as downstream of the catalyst. The high temperature portion of this system is water cooled. A feedback controlled valve at the outlet of the system is used to adjust system pressure. In addition, a view port, shown in Fig. 2, has a video camera for continuous observation of the catalyst including visual assessment of catalyst uniformity.

This system achieves a fuel/air uniformity of ±3% at the catalyst inlet. The system is fully instrumented with catalyst and gas temperatures, pressures, flows and emissions levels that were recorded continuously by a microcomputer data acquisition system. Full emissions analysis including NO_x, CO, UHC, CO_2, and O_2 can be obtained at any location downstream of the catalyst from 7 cm to 160 cm. The fuel was pipeline natural gas as supplied by Pacific Gas and Electric Company through the distribution network. Typical compositions were (mol.-%): methane (95.9), ethane (2.05), propane (0.1), butane (0.03), pentane (0.01), CO_2 (1.42), N_2 (0.48), mercaptan (2–4 ppm).

It should be noted that all of the test data reported in this paper were taken on short inlet stage catalysts. The outlet temperature from these catalysts would be insufficient to initiate homogeneous combustion. Comparison tests in this laboratory have shown that the ignition behavior of multistage catalyst systems are essentially identical to that determined for the inlet stage since the more active inlet stage controls the ignition performance of the catalyst system.

2.2. Methane oxidation rate measurements

The catalyst washcoat powder was scraped from the metal support to measure the specific activity for methane oxidation. Measurements were made at atmospheric pressure in a single pass down flow, tubular reactor of 0.95 cm inside diameter as described previously [5]. The catalyst, typically 50 to 150 mg, was mixed with 1 to 5 g of the support and pressed and sieved to 0.4–0.85 mm particles for the measurement. The reactant gas composition was 2% CH_4 in air and the CH_4 reactant and CO_2 product was analyzed gas chromatographically. Conversions were kept below 10% and the quantity of catalyst adjusted to meet differential conditions at a measurement temperature of 277°C. As reported previously, the catalyst activated with time and reached a steady state activity after 30 to 60 min. The steady state activity, typically achieved at 120 min, was taken as the measure of catalyst activity [5].

2.3. Catalyst preparation

In the tests described in this paper, the catalyst substrate was a corrugated FeCrAl metal foil formed into a monolithic structure (200 to 400 cpsi) with catalyst applied as a thin washcoat layer on the foil. The catalyst was typically Pd on a high surface area mixed oxide support.

3. Ignition/extinction performance

3.1. General behavior

In a gas turbine, the inlet air is compressed to a high pressure, typically in the range of 8 to 20 atm for industrial gas turbines, then fuel is injected and combusted to produce the energy to drive the tur-

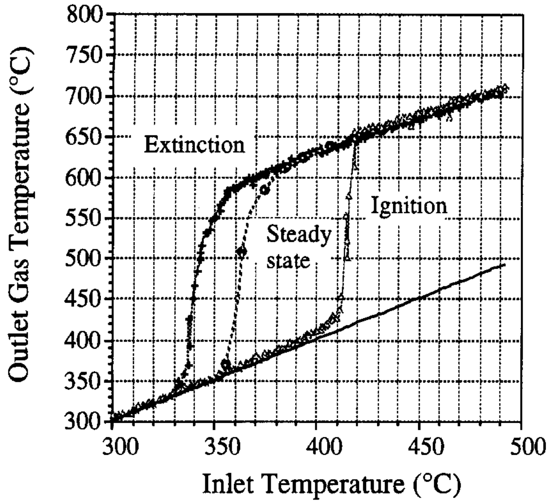

Fig. 3. Ignition/extinction catalyst performance at 11 atm.

bine. One important performance characteristic of a catalytic combustion system is to have good catalytic activity at or very close to the compressor discharge temperature so that the fuel will react on the catalyst to produce the required heat. If the compressor discharge temperature is too low, then some of the fuel must be burned upstream of the catalyst to raise the temperature of the fuel/air mixture entering the catalyst. This combustion will produce NO_x. For this reason, it is desirable to have the catalyst ignition temperature, that is the temperature at which the catalyst will react a large portion of the fuel, below or close to the compressor discharge temperature to eliminate or minimize the need for a preburner that would produce NO_x. The compressor discharge temperature depends on the pressure ratio of the compressor and varies from about 300°C at 9 atm to about 350°C at 12 atm. The preburner is used to start the engine and to bring the gas turbine to operating conditions. At base load, it is desirable to turn the preburner off or as low as possible to minimize NO_x formation in the preburner.

Fig. 3 shows ignition and extinction data for a catalyst at 11 atm pressure and 9300 SLPM for a 50-mm diameter catalyst unit with a fuel/air (F/A, vol methane/vol air ratio) equivalent to an adiabatic combustion temperature (T_{ad}) of 1300°C. The preheat was raised and lowered at 5°C/min with the F/A continuously varied to maintain a T_{ad} of 1300°C and the catalyst exit gas temperature monitored continuously. The ignition temperature, taken as the catalyst inlet temperature at the point of maximum rate of increase in gas temperature, is ca. 414°C, and the extinction temperature is ca. 338°C. In a third measurement, the temperature was decreased stepwise and maintained constant to find the steady state extinction curve. This shows a steady state extinction temperature of ca. 370°C. The large hysteresis between the ignition and extinction temperatures is common in strongly exothermic reaction systems. It occurs in the temperature range where the reactor can exhibit either of two stable operating regimes — a low temperature, low conversion regime or a high temperature, high conversion regime. Starting from a low temperature, the reactor will remain at low conversion until the ignition temperature is reached. Likewise, once ignited, the reactor will maintain high conversion until the temperature drops below the extinction temperature.

In the operation of the gas turbine, the preburner will be used to start the gas turbine and the temperature can then be decreased to the base load operating point. This would suggest that the catalyst can be operated at the inlet temperatures down to the steady state extinction temperature. The specific catalyst shown in Fig. 3 could be operated at temperatures in the range of 380 to 390°C.

A second issue is the effect of combustion products on the ignition/extinction performance of the catalyst system since during preburner turndown, the catalyst inlet will be exposed to high concentrations of H_2O, CO_2 and other minor combustion products. To characterize the influence of preburner product gases, ignition/extinction tests were done first with only electrical preheating and subsequently with the preburner providing a 200°C temperature rise. Tests were done at 11 atm and 9300 SLPM and a constant T_{ad} of 1300°C. The data from these tests are contained in Table 1. The performance shift is small, 18°C for ignition and 12°C for extinction. Table 2 contains data for a less active catalyst at pressures from 1 atm to 11

Table 1
Ignition/extinction tests with preheater only and with preburner at 11 atm

Condition	Ignition temperature (°C)	Extinction temperature (°C)
Electric heater only	422	352
Plus 200°C preburner	440	364
— shift	18	12

Table 2
Effect of pressure and gas velocity on ignition performance

Conditions		Ignition temperature (with electric heater) (°C)
Pressure (atm)	Air flow (SLPM)	
1	1500	350
1	5000	475
4	5000	460
8	7500	470
11	9300	472

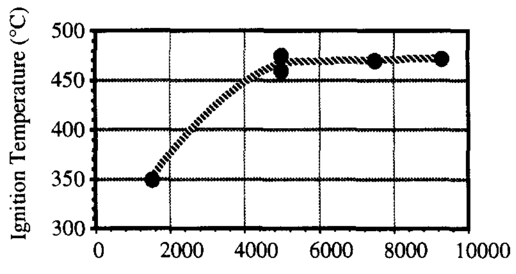

Fig. 4. Effect of mass flow on ignition temperature.

atm and with higher gas velocities as the pressure is increased. In these data, the preburner has a very large effect at low pressure and flow while at higher pressure, the effect of the preburner is small in agreement with the data of Table 1. Work just published from this laboratory shows that H_2O inhibits methane oxidation at approximately -1 order and CO_2 inhibits at approximately -2 order above about 0.005 mol fraction at 277°C [5]. At the conditions used here, 200°C temperature rise from the preburner results in a CO_2 concentration of 0.0085 mol fraction and a H_2O concentration of 0.016 mol fraction at the catalyst inlet. This is in the concentration range where strong inhibition by CO_2 and H_2O was observed. However, the inhibition is probably strongly temperature dependent and at 350 to 400°C, the inhibition may be significantly reduced. As improved catalysts are developed and the ignition/extinction temperature at high pressure is further decreased, this product inhibition of the rate of methane oxidation may become a more important issue.

In another series of tests on a different catalyst sample, the effect of mass flow rate and pressure were evaluated. These data are shown in Table 2 where the ignition temperature was measured for mass flow rates from 1500 to 9300 SLPM and pressures from 1 to 11 atm. The catalyst sample was shown to have a stable activity by reproduction of the initial low mass flow results after the series was completed. Due to system limitations, the pressure had to be increased as the mass flow was increased. However, runs at 1 and 4 atmosphere at 5000 SLPM showed that ignition is only weakly dependent on pressure. As mass flow increases, the ignition temperature rises substantially and appears to become constant. The ignition temperature is plotted versus total mass flow in Fig. 4. Measurements at low pressure and low mass velocity are not indicative of the required performance at the gas turbine operating conditions.

3.2. Correlation of catalyst activity and ignition temperature

A number of different monolithic catalysts were tested for ignition performance at the high-pressure gas turbine operating conditions described above. The washcoat catalyst layer was also removed from the metal foil support and this powder tested for catalytic activity under differential reaction conditions using the procedure described in Section 2.2. These data are presented in Fig. 5. The ignition temperature correlates very well with the catalytic activity of the washcoat over a 200 fold variation in catalyst activity. Catalysts with ignition temperatures as low as 320°C have been demonstrated, approaching the compressor discharge temperature of gas turbines with pressure ratios of 10/1. The extinction temperature for

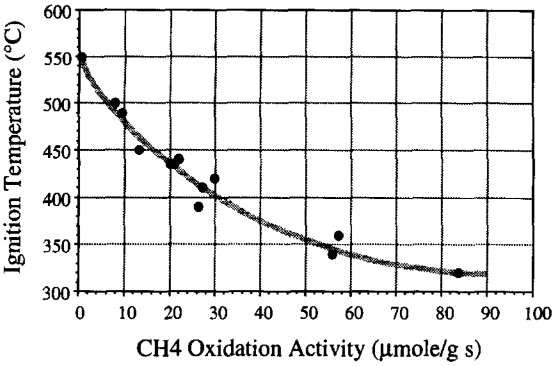

Fig. 5. Correlation between the monolithic catalyst ignition temperature and the specific activity of the washcoat.

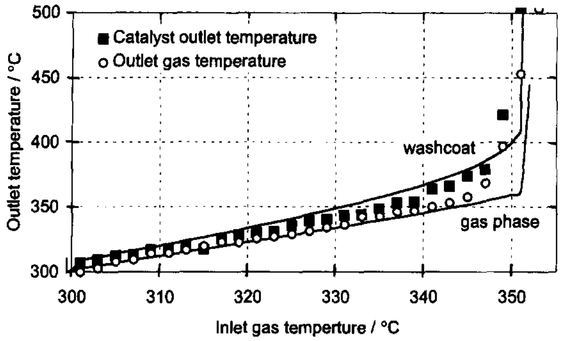

Fig. 6. Comparison of simulation of ignition process with experimental results. Upper solid line is model calculated outlet catalyst temperature and lower solid line is model calculated outlet gas temperature. Points are experimental data as indicated in the legend.

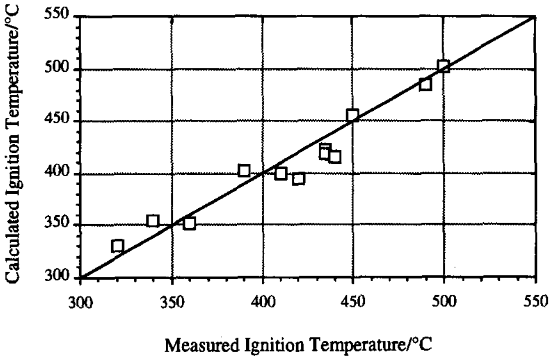

Fig. 7. Correlation of measured ignition temperature with model simulation results.

these catalysts would be approximately 260°C, and could operate at the compressor discharge temperature of turbines with pressure ratios as low as ca. 8/1.

While the correlation of weight specific catalyst activity with ignition temperature is expected, the functionality of this dependence is extremely important because it could then be used to predict the required activity for a certain target level of performance. A reaction model for this monolithic catalyst configuration was developed. This was a single channel model that incorporated a porous washcoat layer on a nonporous support and a uniform distribution of catalytic sites on the porous washcoat surface. The model assumes that ignition occurs at low methane conversion, therefore the longitudinal (axial) gradients of concentration and temperature can be ignored. With this assumption, mass and heat balances between the inlet and outlet sections can be written as a system of ordinary differential equations following the theory for ignition in heterogeneous systems developed by Frank-Kamenetskii [6]. The assumption that axial gradients of concentration and temperature can be ignored is reasonable since the ignition phenomenon occurs at very low conversion. Only after the ignition process has been defined does the conversion and heat release become significant and this model no longer applies. To describe the ignition phenomenon, those equations were solved to obtain the outlet gas and washcoat temperatures when the inlet gas temperature increases linearly with time. A plot of the outlet gas temperature versus the inlet gas temperature will generate an ignition curve similar to that shown in Fig. 3.

Using the measured catalyst activity, an activation energy of 70 kJ/mol, a kinetic rate expression for CH_4 oxidation that is 0.47 order in CH_4 and zero order in O_2, the model produced the ignition curve shown in Fig. 6 for a selected catalyst sample with an activity of $60 \cdot 10^{-6}$ mol/g s and a measured ignition temperature of 350°C. The agreement between the model and the measured ignition curve is very good. This model predicts the ignition performance over most of the catalyst activity range as shown in Fig. 7. The data suggest that the ignition behavior is a well understood phenomenon that is controlled by catalyst activity and mass and heat transfer to the reacting surface. This model can be a very useful tool for prediction of ignition behavior.

4. Conclusions

Ignition and extinction of metal monolith honeycomb supported Pd catalytic combustion catalysts shows a substantial hysteresis, most likely due to multiple steady states for this strongly exothermic system. However, this phenomenon needs further study. Ignition does show some product inhibition, albeit at a lower level than expected from kinetic rate measurements at low temperature and low conversion. To fully understand the importance of product inhibition, the temperature dependence of product inhibition should to be measured.

A reaction model for a single channel honeycomb catalyst can reproduce ignition behavior observed for real sub-scale monolithic honeycomb catalysts operated at realistic high pressures and high gas velocities typical of gas turbine combustors. This model uses the specific catalyst activity measured for the washcoat powder under differential conditions and can accurately predict the ignition behavior of the monolithic catalyst. This model has been shown to reproduce measured behavior over 200-fold range of activities and should provide a useful tool for understanding the importance of catalyst design parameters.

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