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Catalytic combustion over platinum group catalysts: fuel-lean versus fuel-rich operation

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Abstract

Performance data are presented for methane oxidation on alumina-supported Pd, Pt, and Rh catalysts under both fuel-rich and fuel-lean conditions. Catalyst activity was measured in a micro-scale isothermal reactor at temperatures between 300 and 800 °C. Non-isothermal (near adiabatic) temperature and reaction data were obtained in a full-length (non-differential) sub-scale reactor operating at high pressure (0.9 MPa) and constant inlet temperature, simulating actual reactor operation in catalytic combustion applications.

Under fuel-lean conditions, Pd catalyst was the most active, although deactivation occurred above 650 °C, with reactivation upon cooling. Rh catalyst also deactivated above 750 °C, but did not reactivate. Pt catalyst was active above 600 °C. Fuel-lean reaction products were CO_2 and H_2O for all three catalysts.

The same catalysts tested under fuel-rich conditions demonstrated much higher activity. In addition, a ‘lightoff’ temperature was found (between 450 and 600 °C), where a stepwise increase in reaction rate was observed. Following ‘lightoff’ partial oxidation products (CO, H_2) appeared in the mixture, and their concentration increased with increasing temperature. All three catalysts exhibited this behavior.

High-pressure (0.9 MPa) sub-scale reactor and combustor data are shown, demonstrating the benefits of fuel-rich operation over the catalyst for ultra-low emissions combustion.

Keywords: Catalytic combustion; Gas turbine; Methane oxidation; Reaction mechanism

1. Introduction

Catalytic combustion is one means of meeting increasingly strict emissions requirements for industrial and utility gas turbines. Natural gas is currently the fuel of choice for power-generating gas turbines, and therefore catalytic combustion of methane has been the focus of interest in recent years. By enabling stable low-temperature combustion (as low as 1200 °C), NO_x emissions from natural-gas-fueled catalytic combustors can be below 3 ppm, with single-digit CO/UHC emissions and with low levels of combustor acoustic noise.

For methane oxidation under fuel-lean conditions, Pd-based catalysts are currently the only practical choice, because they can offer acceptable activity, lightoff temperature, and resistance to volatilization [1–3]. Unfortunately Pd–PdO catalyst morphology and its reactions with methane are complex, and lead

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to complex behaviors such as deactivation at high temperature (above about 750 °C) and hysteresis in reaction rate through heating and cooling cycles [4–8]. In addition, lightoff and extinction temperatures are well above 300 °C for fuel-lean reaction on Pd-based catalysts, thus requiring the use of a preburner in many engine applications [9,10].

A further difficulty is encountered in the form of oscillations in activity and temperature of Pd-based catalysts. These have been observed for fuel-lean reaction of methane under constant inlet conditions [11–14]. A typical example of such oscillatory behavior is shown in Fig. 1, as observed in our laboratory at atmospheric pressure. Here, a fuel-lean mixture of methane and air (0.5 equivalence ratio) entered a catalytic reactor at about 525 °C gas temperature and 30 m/s velocity. The catalyst was a mixture of Pt and Pd with 75 wt.% Pd, which was applied to a sintered γ-alumina washcoat by incipient wetness. The washcoat was bonded to an underlying metal substrate, which was backside cooled by a constant-flow gas stream. In the figure, large amplitude oscillations in catalyst temperature ($\Delta T > 200\,^{\circ}\mathrm{C}$) are observed with a period on the order of 5–10 min, despite constant inlet conditions. Note also that the upstream catalyst temperature ($T_{\mathrm{surface\,1}}$) is out of phase with the downstream temperature ($T_{\mathrm{surface\,2}}$), so that the gas stream temperature at the reactor exit varies only slightly in time ($\Delta T < 20\,^{\circ}\mathrm{C}$). While we do not have a complete understanding of this complex behavior, we attribute it to dynamics of Pd–PdO transition under fuel-lean operating conditions. Oscillations such as this are disadvantageous in a catalytic combustion system, where temperature swings lead to life-limiting thermal cycling of catalyst, support, and substrate, as well as unpredictable combustion performance downstream of the catalyst. A catalyst system with more stable and predictable behavior is desired.

In addition to catalyst challenges, commercial acceptance of catalytic combustion by gas turbine manufacturers and by power generators has been slowed by the need for durable substrate materials. Of particular concern is the need for catalyst substrates which are resistant to thermal gradients and thermal shock [9,15,16]. Metal substrates best fill this need, but their temperature must be limited to less than 1000 °C to assure sufficient material strength and long life. Downstream of the catalyst, combustion temperatures greater than about 1200 °C are required for gas-phase reactions to complete the burnout of fuel and CO in

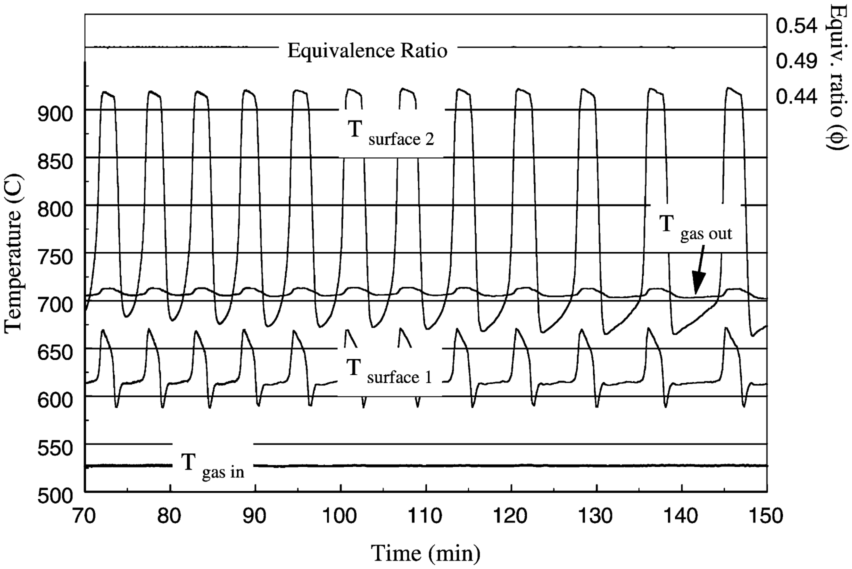

Fig. 1. Oscillations in catalytic reactor operating under fuel-lean conditions. Pd-based catalyst. Inlet gas temperature, 525 °C; flow velocity, 30 m/s; and ϕ, 0.5 all constant. $T_{\mathrm{surface\,1}}$ is catalyst temperature at the upstream end of the catalyst bed, $T_{\mathrm{surface\,2}}$ is catalyst temperature at the mid-bed.

a reasonable residence time (on the order of 10 ms). Thus, only a portion of the fuel can be reacted on the catalyst. A major challenge, then, is to limit the extent of reaction within the catalyst bed such that excessive heat does not damage the catalyst or substrate, yet release sufficient heat that downstream gas-phase combustion is stabilized at low flame temperatures for ultra-low emissions.

In fuel-lean systems, two different methods are commonly used to limit the extent of reaction, and to moderate catalyst temperature: (1) catalyst activity cut-off—this method relies upon an intrinsic decrease in catalyst activity at high temperature, generally caused by a reversible Pd–PdO transformation; and/or (2) flow channeling in combination with catalyst cooling—here, a portion of the reactant stream contacts the catalyst, while the remainder is channeled into non-catalytic passages in thermal contact with the catalyst, thus cooling the catalyst. For both of these cases, however, it is imperative that gas-phase reactions do not occur within the catalyst bed (including cooling passages), since this implies a loss of reaction limitation and ultimate over-temperature and failure of the catalyst bed. Preventing such gas-phase reactions has been especially challenging in applications to new, high-firing temperature turbines, where fuel/air ratios in the catalyst bed are well within the flammability limits. Failure can then occur by flashback from the downstream combustor or by auto-ignition.

An alternative means to limiting the extent of reaction is to operate the catalyst fuel-rich. In this scenario, there is insufficient oxygen to fully oxidize all fuel in the catalyst bed, and the extent of reaction is limited even if gas-phase reactions occur. To use a fuel-rich catalyst bed in a catalytic combustion system, additional air is introduced downstream of the catalyst so that combustion completion can occur fuel-lean. Based on this concept, fuel-rich catalytic reactors were tested by NASA and contractors for liquid fuel applications, and showed good soot-free performance [17,18]. An examination of fuel-rich catalysis on a variety of liquid fuels was also conducted at Yale University, under support from NASA [19]. Like the NASA results, this work showed soot-free catalyst performance on a range of fuel types, including a surrogate jet fuel. United Technologies Research Center [20] also investigated fuel-rich catalytic reaction of liquid fuels, to reduce downstream thermal NO_x generation by removing some heat of reaction prior to gas-phase combustion.

For these liquid fuel applications, ultra-low NO_x emissions (<3 ppm) have not been considered feasible because of these fuels propensity for auto-ignition during mixing with additional combustion air downstream of the catalyst. Even for natural gas fuel, previous systems have not permitted mixing of raw catalyst effluent with additional combustion air. For example, Acurex tested a two-stage natural gas combustion system having a fuel-rich catalyst stage followed by inter-stage heat extraction [21]. Additional combustion air was introduced only after heat extraction, and prior to a final fuel-lean catalytic combustion stage.

Recently, however, we have tested a catalytic combustion system using fuel-rich catalytic reaction followed by lean-premixed combustion, without inter-stage heat extraction and without incurring auto-ignition [22,23]. The approach is shown schematically in Fig. 2. Combustion air (as from a gas turbine

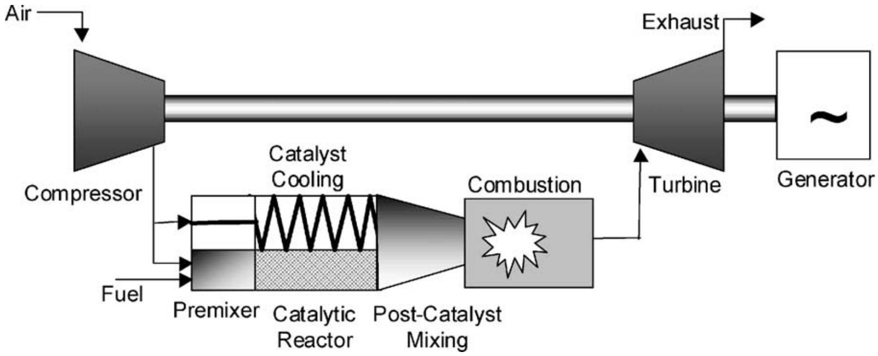

Fig. 2. Schematic diagram of fuel-rich catalytic reactor in lean-combustion system.

compressor) is split into two portions. The smaller portion is mixed with all fuel to form a fuel-rich mixture, and is reacted in contact with a catalyst. The larger portion is used to cool the catalyst, and is then mixed with the fuel-rich reaction effluent downstream of the catalyst, to produce a fuel-lean, reactive mixture. Catalyst cooling moderates the temperature of the fuel-rich reaction effluent, such that gas temperatures in the post-catalyst mixing zone allow more than 10 ms before auto-ignition. Thus, near-perfect mixing can be achieved before the onset of homogeneous combustion, allowing downstream combustion to take place in a lean-premixed mode, with ultra-low NO_x emissions. We call this approach rich catalytic/lean-burn (RCL^{TM}) combustion.

In this paper, we present comparative data on catalyst performance under fuel-lean and fuel-rich conditions and show that fuel-rich operation provides greater catalyst activity, lower catalyst lightoff and extinction temperatures, and wider choice of catalyst type. Data are shown for Pt, Pd, and Rh catalysts. We also discuss operation of the fuel-rich catalytic reactor, and present sub-scale high-pressure (0.9 MPa) catalytic combustor test results demonstrating ultra-low NO_x lean-premixed combustion downstream of fuel-rich catalytic reaction.

2. Isothermal reactor experiments and results

To compare catalyst activity for oxidation of methane under fuel-lean versus fuel-rich conditions, Pt, Pd, and Rh catalysts were separately tested in an isothermal micro-scale reactor, as shown schematically in Fig. 3. Each catalyst was supported on stabilized γ-alumina, and each had equivalent precious metal loading on a weight basis. The reactor was similar to that described in Lyubovsky and Pfefferle [24]. A strip of catalyst 6.4 mm long (in the streamwise direction) and about 12 mm wide (in the cross-stream direction) was applied to the middle of a thin metal coupon. The coupon was then placed between two electrically heated metal blocks, in thermal contact with the bottom block. The top block had a 0.5 mm gap to allow for flow of the reactant mixture over the catalyst. Catalyst temperature was measured by a thermocouple contacting the backside of the coupon, opposite the catalyst, and was controlled by electric heaters. By this means, catalyst temperature was externally controlled, and was made independent of the reaction rate and heat release on the catalyst (isothermal operation).

For the tests reported here space velocity was held constant at about 7.4×10^6 l/h, giving a catalyst contact time of about 0.5 ms. Note that N_2, O_2 and CH_4 flow were separately controlled prior to mixing at the reactor inlet. Gas samples were extracted from the inlet and exit of the reactor, and were analyzed by a gas chromatograph (GC).

For each catalyst type, the same catalyst sample was tested under both fuel-rich and fuel-lean conditions. The fuel-rich test was performed first, followed by the fuel-lean test, because high-temperature deactivation was not observed for any of the catalysts under fuel-rich conditions (as discussed below). Test conditions are shown in Table 1, including modified equivalence ratio $\Phi = 1/(\phi + 1)$ (as introduced by Schmidt and co-workers [25]). Unlike conventional equivalence ratio ϕ, the modified equivalence ratio Φ is bounded between 0 and 1, and is symmetric about the stoichiometric point of 0.5, having an equal range of values on both the fuel-rich ($\Phi < 0.5$) and fuel-lean ($\Phi > 0.5$) sides. Two gas compositions were selected for testing, one at $\Phi = 0.25$ in the 'middle' of the

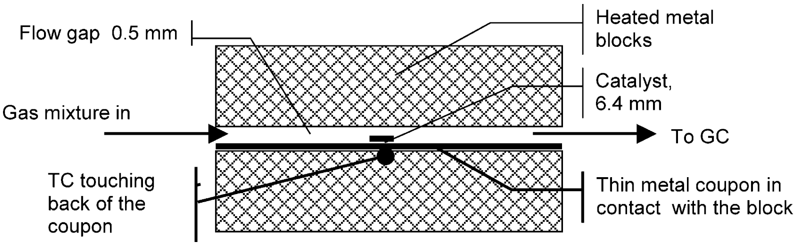

Fig. 3. Schematic of micro-scale isothermal reactor for testing catalyst activity.

Table 1
Conditions for comparing catalyst performance in fuel-lean and fuel-rich operation

	Lean	Rich
Equivalence ratio, ϕ	0.33	3
$\Phi = 1/(\phi + 1)$	0.75	0.25
Gas composition, $CH_4/O_2/N_2$ (%)	3.2/19.4/77.4	3.2/2.2/94.6
Space velocity (h^{-1} @RT)	7.4×10^6	7.4×10^6
Contact time (ms)	0.5	0.5
Temperature ramp (°C/min)	2	2

fuel-rich 'mixture composition space', and one at $\Phi = 0.75$ in the 'middle' of the fuel-lean 'mixture composition space'. Nitrogen content was selected to provide a fuel-lean mixture equivalent to 3.2% of CH_4 in air. For fuel-rich testing, the oxygen flow was decreased and substituted by nitrogen, such that the methane concentration and the overall flow rate remained constant under both fuel-rich and fuel-lean conditions. Therefore, methane conversion observed in the test was a direct measure of catalyst activity. To measure the temperature dependence of catalyst activity the reactor temperature was increased at the rate of 2 °C/min from 300 to 800 °C, then held at 800 °C for 2 h, and then decreased back to 300 °C at the rate of 2 °C/min.

A comparison of methane conversions for all three catalysts, under both fuel-rich and fuel-lean conditions, is shown in Fig. 4. The solid symbols represent data obtained during the heating cycle, and the open symbols represent data obtained during the cooling cycle. It was found that for all tested catalysts methane conversion was much higher under fuel-rich conditions than under fuel-lean conditions.

Fig. 5 shows greater detail of the same fuel-lean methane conversion data, with data for all three catalysts plotted on the same graph. Again, the solid symbols represent data obtained during the heating cycle, and the open symbols represent data obtained during the cooling cycle. Comparing the behavior of the different catalysts under fuel-lean conditions, it is seen that Pd catalyst exhibits the highest activity at low temperature but deactivates above about 650 °C. On the cooling cycle, reactivation of Pd catalyst is observed as temperature is decreased from 800 to 600 °C. This hysteresis behavior is consistent with the properties of Pd catalysts reported in the literature [5,7]. Rhodium catalyst shows activity similar to Pd at low temperature and remains active to higher temperatures (about 750 °C), such that the peak activity for Rh (near 6% conversion at 750 °C) exceeds the peak activity for Pd (just over 4% conversion at 650 °C). Deactivation of

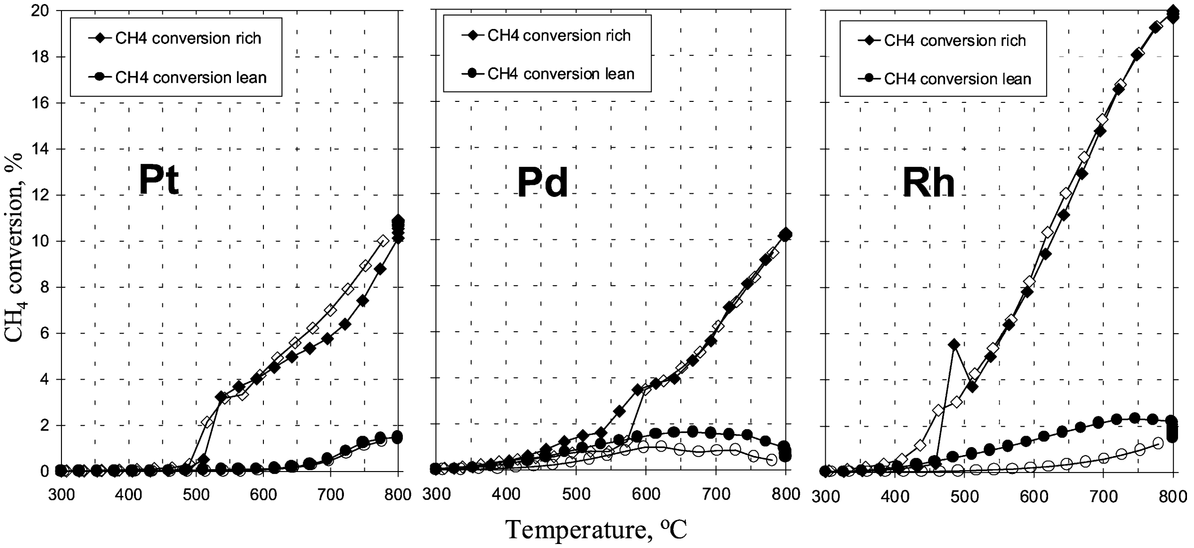

Fig. 4. Catalyst activity for methane oxidation under fuel-rich and fuel-lean conditions. Same weight loading of the catalysts. Filled symbols: heating cycle, empty symbols: cooling cycle.

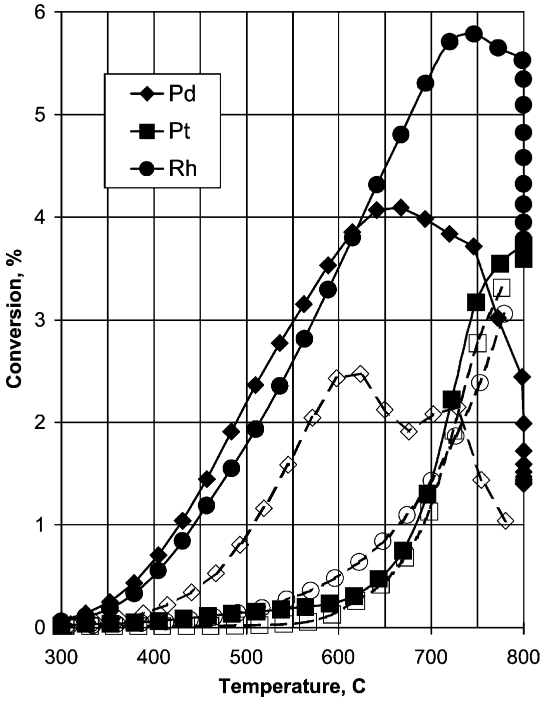

Fig. 5. Catalytic conversion of methane, for fuel-lean reacting conditions, on Pt, Pd, and Rh catalysts. Same weight loading of the catalysts. Filled symbols: heating cycle, empty symbols: cooling cycle.

the Rh catalyst, however, is irreversible: no reactivation is observed on the cooling cycle. Platinum catalyst remains active at high temperature, and does not show deactivation or hysteresis behavior. However, Pt has the lowest activity of the three tested catalysts at low temperature (less than about 700 °C). No partial oxidation products were observed in the product mixture under fuel-lean conditions for any of the three catalysts at any point in the temperature cycle.

Under fuel-rich conditions the behavior of all three catalysts changed significantly. For all three catalysts, conversion remained low (less than 2%) at temperatures below about 450 °C and closely coincided with conversion under the fuel lean conditions. Between 450 and 600 °C, though, each catalyst exhibited a ‘lightoff’, where a stepwise increase in reaction rate is observed. Note that this ‘lightoff’ is not a thermal event (is not an effect of heat release on the catalyst surface) since the catalyst is in good thermal contact with the temperature-controlled electrically heated metal block. Thus, the observed stepwise increase in reaction rate occurred with incremental increase in catalyst temperature. Similar behavior was reported by Burch and Loader [26] for Pt catalyst under fuel-rich conditions, where they observed this type of ‘lightoff’ event at about 450 °C. In our tests, ‘lightoff’ occurred at about 540 °C for Pt catalyst, at about 560 °C for Pd catalyst, and at about 480 °C for Rh catalyst.

Composition of the exit gas mixture in a fuel-rich test over Pt catalyst is shown in Fig. 6. Note that concentrations of H_2, O_2, CH_4, CO and CO_2 were directly measured by a GC, while water concentration was calculated from the atomic balance. Mixture compositions in the tests over other catalysts were in general similar to this one and are not shown here in detail. It was found that prior to catalyst ‘lightoff’ only CO_2 and H_2O were detected in the fuel-rich reaction product stream. Immediately after the ‘lightoff’ trace amounts of CO and H_2 were also detected, although CO_2 and H_2O remained the predominant reaction products. As the reactor temperature was further increased the concentration of CO_2 in the product stream remained the same or even decreased, while the concentration of CO rapidly increased, indicating an overall increase in the reaction rate and process selectivity to partial oxidation products. Note that while CO concentration was increasing at higher temperatures after the ‘lightoff’, H_2 concentration remained at a trace level. This contradicts thermodynamic analysis, which predicts that the amount of H_2 in the product should be about twice that of CO. We attribute this discrepancy to the gas-phase oxidation of H_2 by remaining molecular oxygen downstream of the catalyst. The construction of the rig and the sampling probe is such that there was a significant cavity in the downstream region of the rig from which the gas was sampled. Residence time of the gas stream, still at the reactor temperature in this cavity was about 5 ms, which was sufficient for gas-phase oxidation of molecular hydrogen at temperatures above 500 °C. This is consistent with our observations that at similar tests conducted at lower space velocities, when near 100% of free oxygen was consumed over the catalyst, H_2 concentration in the reaction product stream was about twice that of CO at temperatures above the ‘lightoff’. Therefore, CO concentration in the product stream was used as a measure of the reaction selectivity towards partial oxidation products.

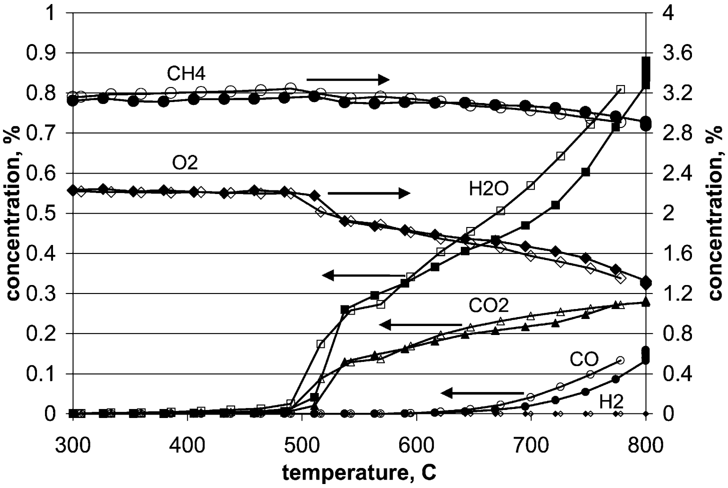

Fig. 6. Exit gas composition dependence on temperature for the fuel-rich test over the Pt catalyst. Filled symbols: heating cycle, empty symbols: cooling cycle.

Similar temperature dependence (with some differences in the ‘lightoff’ temperature and overall process selectivity) was characteristic for all three of the tested catalysts. Selectivity to CO together with methane conversion under fuel-rich conditions is shown Fig. 7. Under fuel-rich conditions Rh catalyst showed the highest activity and the highest selectivity to partial oxidation products at temperatures above about 450 °C (after Rh ‘lightoff’). This is consistent with the observations of Hickman et al. [27], who reported that Rh catalyst was more selective to partial oxidation products than Pt catalyst in partial oxidation of methane under short contact time conditions. The data in Fig. 7 also shows that no high-temperature deactivation was observed under fuel-rich conditions for Pt, Pd, or Rh catalysts. This stands in contrast to the fuel-lean test results, where Pd and Rh catalysts showed significant deactivation during the 2 h hold period at 800 °C. Fig. 7 also

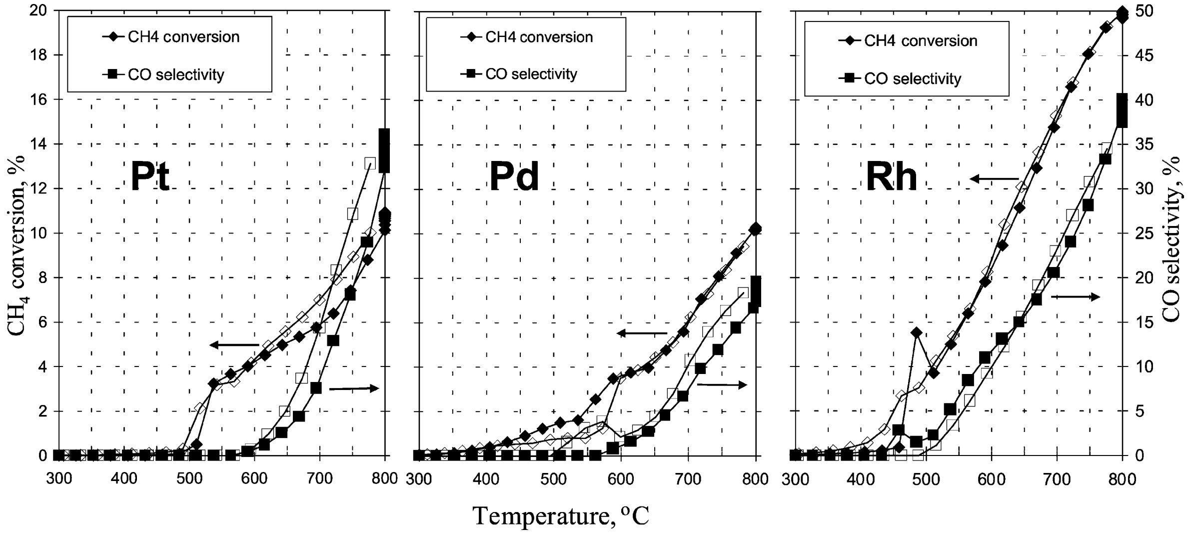

Fig. 7. Methane conversion and CO selectivity under fuel-rich conditions. Same weight loading of the catalysts. Filled symbols: heating cycle, empty symbols: cooling cycle.

shows that under fuel-rich conditions the heating cycle and cooling cycle activity curves for each catalyst are nearly coincident at high temperature, and only a small hysteresis was observed at the ‘lightoff’ temperature for each catalyst. Surprisingly, though, there was an increase in CO selectivity on the cooling cycle over the Pd catalyst, similar to Pd catalyst activation on the cooling cycle under fuel-lean conditions. Apparently these phenomena are related and suggest that Pd catalyst starts to re-oxidize at low temperatures even under the fuel-rich conditions of this test.

3. Adiabatic reactor experiments and results

Properties of fuel-rich catalytic combustion of methane were further studied under near-adiabatic conditions for Rh catalyst supported on stabilized γ-alumina washcoat over a 0.6 cm long metallic honeycomb monolith substrate. All channels of the honeycomb were catalyst coated, and the catalyst was not externally heated or cooled (and thus operated under near adiabatic conditions). A preheated methane/air mixture passed over the catalyst at a linear flow velocity of about 50 m/s, corresponding to a contact time of about 0.1 ms. Temperature of the inlet gas was measured by a radiation shielded thermocouple upstream of the monolith. To measure catalyst temperature a thermocouple was placed inside one channel of the honeycomb, and the channel was then blocked with ceramic paste to prevent convective heat loss from the thermocouple bead.

Fig. 8 shows inlet gas temperature ($T_{\text{inlet gas}}$) and temperature of the Rh catalyst (T_{monolith}) during a heating and cooling cycle at a constant $\phi = 5.0$ fuel-rich equivalence ratio. At the highest inlet temperature (430 °C) the temperature rise on the catalyst was about 460 °C, giving a catalyst temperature just under 900 °C. At the lowest inlet temperature (290 °C), the temperature rise on the catalyst was about 550 °C. Thus, there was greater heat release at the catalyst surface for lower inlet gas temperatures. This effect is due to decreasing yield of the partial oxidation products at lower temperature under fuel-rich reaction conditions, as shown earlier in Fig. 7. Under fuel-rich conditions, two parallel reactions take place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,$$
$$\Delta H = -802\,\text{kJ/mole}$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2,$$
$$\Delta H = -36\,\text{kJ/mole}$$

The first reaction (complete oxidation) is highly exothermic, while the second reaction (partial oxidation) provides very little heat release. The data

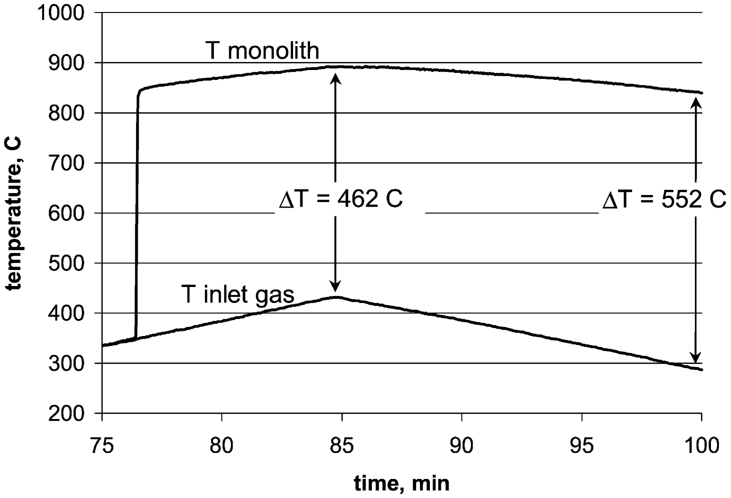

Fig. 8. Effect of the inlet gas temperature variation on the catalyst surface temperature. Rh supported on stabilized γ-alumina on 0.6 cm long metallic monolith. $\phi = 5.0$; linear flow velocity, 50 m/s; $\tau \sim 0.1$ ms.

in Figs. 7 and 8 show that for both isothermal and adiabatic reaction conditions, selectivity to partial oxidation products increases with increasing catalyst temperature. This results in lower heat release on the catalyst surface per mole of converted methane, stabilizing the catalyst temperature over changing inlet conditions.

4. Non-isothermal (backside-cooled) reactor experiments and results

A full-length (non-differential) catalytic reactor was fabricated and tested under fuel-rich conditions at 0.9 MPa pressure. This reactor was nominally 1.9 cm in diameter, and represented a sub-scale version of an RCL™ catalytic combustor reactor. The substrate was backside-cooled on the non-catalytic side with pure air (no fuel), and this cooling air was then mixed with the fuel-rich catalyst effluent downstream of the catalyst to create a fuel-lean mixture for complete burnout of all fuel. The overall equivalence ratio ϕ is defined as the ratio of fuel to total air (i.e. air going through the catalytic side and the cooling side of the reactor combined). Note that the reactor operates under near adiabatic conditions with respect to the combined catalyst and cooling air flows, that is, when the cooling air is considered to be a portion of the reactor flow. With respect to the catalytically reacted mixture alone, however, reaction is not adiabatic and heat removal must be considered when calculating equilibrium gas compositions and temperature.

Fig. 9 shows data obtained for this reactor over a 3 h period operating on commercial-grade natural gas (bottled). Between time 0 and 30 min, the inlet temperature (labeled $T_{\text{gas in}}$) was gradually increased to a steady-state value of 400 °C, while holding a constant overall equivalence ratio of $\phi = 0.5$. At 380 °C the catalyst lit off, as shown by the rise in catalyst temperature (T_{catalyst}) from 380 to 780 °C. At time 80 min the equivalence ratio was increased from 0.5 to 0.6, giving a slight decrease in catalyst temperature (to 790 °C) as the fuel-rich mixture contacting the catalyst moved further from stoichiometric (became more fuel-rich). At time 120 min the equivalence ratio ϕ was decreased from 0.6 to 0.4, and the catalyst temperature increased slightly to about 820 °C. Note that for fuel-rich operation of this catalyst, a 33% change in equivalence ratio (from 0.6 to 0.4) gives less than 10% change in catalyst temperature rise (from 390 °C to 425 °C above inlet temperature). In general, we find that for fuel-rich operation catalyst temperature is significantly less sensitive to variations in combustor equivalence ratio than for fuel-lean catalyst operation, because reaction (and heat release) is limited by deficit of oxygen; this reduced sensitivity provides a significant

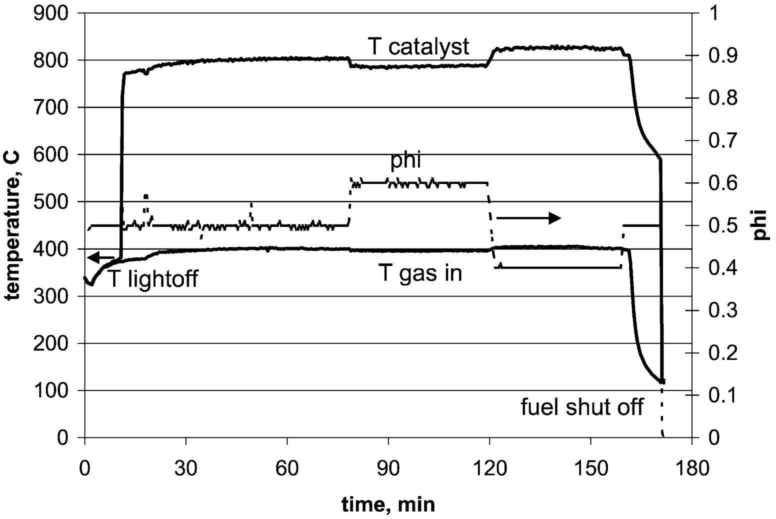

Fig. 9. Lightoff, extinction, and steady-state performance data for a sub-scale fuel-rich catalytic reactor operating at 0.9 MPa on bottled commercial-grade natural gas.

Table 2
Summary of effect of variation in fuel-rich equivalence ratio on selectivity and conversions of both methane and oxygen, for full-length, backside-cooled catalytic reactor

$\Delta\phi$	ΔT_{cat}	CO, H_2 yield (%)	ΔCH_4 conversion (%)	ΔO_2 conversion (%)
Threefold decrease	60 °C increase	Fourfold increase	Fourfold increase	Near constant

operational advantage for fuel-rich catalytic combustion systems.

At time 160 min the equivalence ratio was increased to 0.5 again, and the inlet temperature was then gradually decreased to 120 °C over a 10 min period (electric air heater was shut off and the inlet section was cooling down). Note that at 120 °C inlet temperature the catalyst remained lit off, with a catalyst temperature of 590 °C (470 °C above inlet temperature), until the fuel was shut off. Thus, the catalyst extinction temperature was below 120 °C (and was not measured exactly during this test), and was far below the 380 °C lightoff temperature. Again, in general we find that for fuel-rich operation catalyst extinction temperature at realistic operating conditions (near-adiabatic) is far below the catalyst lightoff temperature. This is especially advantageous in ultra-low NO_x catalytic combustion applications, where the ability to remain lit at low inlet temperature avoids the need for NO_x-generating preburner operation.

Additional testing was conducted on the full-length, backside-cooled catalytic reactor geometry. Of particular interest is the effect of variation in equivalence ratio on selectivity and conversions of both methane and oxygen. Directional trends from these tests are summarized in Table 2. Data were obtained via GC analysis of gas samples from the downstream end of the catalytic section, prior to mixing with cooling air. Note that oxygen conversion remained essentially constant over a broad range of equivalence ratios (consistent with oxygen mass transfer limitation of reaction), yet methane conversion and selectivity to partial oxidation products (CO and H_2) were highly sensitive to fuel-rich equivalence ratio and increased at leaner mixtures, even with only about 60 °C change in catalyst temperature over the range of tested equivalence ratios.

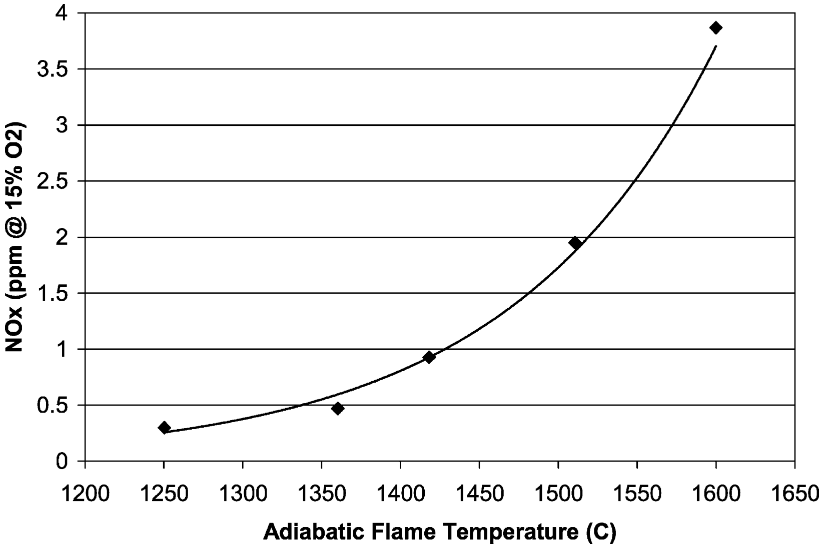

Fig. 10. NO_x emissions obtained after complete fuel-lean combustion following mixing of catalyst effluent with catalyst cooling air downstream of sub-scale fuel-rich catalytic reactor operating on bottled commercial-grade natural gas. CO emissions were less than 1 ppm for all conditions. Inlet temperature, 425 °C; peak catalyst temperatures, 750–800 °C; pressure, 0.9 MPa.

Fig. 10 presents NO_x emissions obtained after complete combustion downstream of the full-length, backside-cooled catalytic combustor, operating on commercial-grade natural gas (bottled). CO emissions were less than 1 ppm for all conditions shown. The reactor and combustor were operated at 0.9 MPa pressure, and combustion occurred under fuel-lean conditions following mixing of catalyst effluent with catalyst cooling air. Inlet temperature to the catalyst was 425 °C, and peak catalyst operating temperatures were between 750 and 800 °C. All cooling air was mixed with catalyst effluent, and no additional air was introduced. Combustion took place inside a 5 cm diameter insulated ceramic tube. Thus, the nominal 1.9 cm diameter reactor was followed by a sudden expansion (dump) for flame stabilization, after mixing of catalyst effluent with catalyst cooling air. Emissions samples were extracted after a 32 ms residence time in the downstream combustor. As shown in Fig. 10, NO_x emissions were less than 3 ppm for adiabatic flame temperatures less than 1540 °C, demonstrating that ultra-low-NO_x lean-premixed combustion is achievable downstream of fuel-rich catalytic reaction.

5. Discussion

Interaction of methane molecules with metallic surfaces has been studied by many investigators both under reaction and high-vacuum conditions. It is generally accepted that the initial step in methane activation over a catalytic surface involves assisted hydrogen abstraction with formation of adsorbed hydrogen and methyl radicals [28,29], while further dissociation of the C–H bonds proceeds rapidly all the way to carbon [30,31]. Therefore, activation of a first C–H bond is the crucial step of the methane oxidation reaction [32]. Extremely large isotope effect observed for dissociation probability of CH_4 and CD_4 in experiments on methane adsorption on polycrystalline metal surfaces suggested a tunneling mechanism for the passage of a hydrogen atom to the adsorbed state [33]. From molecular beam experiments on methane adsorption on Ni(1 1 1) single crystal surfaces, Ceyer et al. [31,34] have found that the vibrational and the normal component of translational excitation of methane exponentially increase the probability for dissociative chemisorption to an adsorbed methyl radical and a hydrogen atom. They argue that the deformation of a methane molecule upon impact with the surface results in a proper configuration for the transitional state that leads to the dissociation products. Close geometric coordination between the methane molecule and the metallic surface is required in order to make the potential barrier thin enough to allow tunneling of a proton into the product state. Valden et al. [35,36] showed that the rate of methane adsorption on the Pd(1 1 0) surface decreases linearly as the oxygen coverage is increased up to 0.4 ML, which is in agreement with the first order Langmuir kinetics when two active sites are blocked by one oxygen atom. These findings suggest that methane dissociation probability strongly depends on the geometric correlation between the molecule and the metal surface. Therefore, rate of methane conversion over the catalyst should be strongly influenced by a structure of the metallic surface and on its coverage with the intermediate species.

Summarizing the results reported above we have observed the following properties of catalytic combustion of methane under fuel-rich conditions.

Isothermal reactor:

- On the heating cycle methane conversion increases stepwise at a ‘lightoff’ point without step change in the catalyst temperature.
- Only CO_2 and H_2O are found in the product mixture below the ‘lightoff’ point, while rapidly increasing amounts of partial oxidation products are observed at higher temperatures.

Adiabatic reactor:

- Variation in catalyst surface temperature is significantly smaller than variation in inlet gas temperature.

Backside-cooled reactor:

- CH_4 conversion increases at higher catalyst temperature and lower fuel-rich equivalence ratio, while O_2 conversion remains nearly constant.
- Selectivity to partial oxidation products increases at higher catalyst temperature and lower fuel-rich equivalence ratio.

These observations suggest a different state of the catalyst surface under fuel-rich conditions than under fuel-lean conditions, resulting in a different

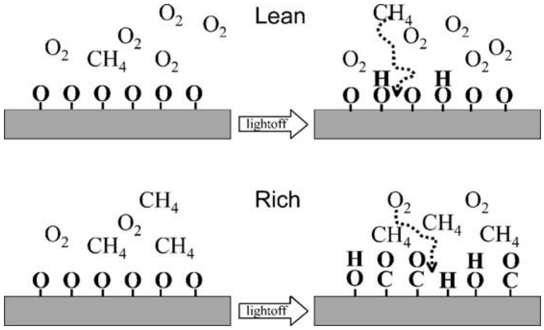

Fig. 11. Schematic mechanism for the catalyst performance under fuel-lean and fuel-rich operating conditions.

mechanism of methane interaction with the catalyst. This is shown schematically in Fig. 11.

In the fuel-lean approach to catalytic combustion lightoff is usually referred to as a stepwise transition of the catalytic reaction from kinetically limited to mass transfer limited operation [37]. This transition leads to a rapid increase in methane conversion, heat release and catalyst temperature (surface temperature rises to the adiabatic combustion temperature if no external cooling of the catalyst is provided). Before the lightoff, gas composition over the catalyst is about the same as that in the bulk of the flow. Activation of methane on the catalyst surface is the limiting step [34], while adsorption of oxygen is fast and proceeds without significant activation barrier. The catalyst surface is, therefore, covered by oxygen either as adsorbed adatoms or in some form of metal oxide species [38,39].

Because of the excess oxygen in the gas mixture under fuel-lean conditions, methane diffusion to the catalyst surface becomes the limiting step after the lightoff. Concentration of methane over the catalyst becomes essentially zero and the catalyst surface remains covered by oxygen (and likely some OH) species. Carbon and hydrogen species which form on the surface as a result of methane dissociation are immediately oxidized to CO_2 and H_2O by surrounding oxygen.

Under fuel-rich conditions oxygen becomes the limiting reactant. At low temperatures, however, when the process is kinetically limited, the reaction mechanism is similar to that under fuel-lean conditions. Oxygen adsorption is much faster than that of methane, and oxygen species cover the surface despite the lower oxygen concentration in the gas phase. Methane molecules, which dissociate on the catalyst are completely oxidized to CO_2 and H_2O, such that only complete oxidation products are observed in the mixture. This is consistent with observed similarity in catalyst activity in lean and rich tests at low temperatures.

After fuel-rich ‘lightoff’, however, the reaction mechanism becomes significantly different. Because oxygen is now the limiting reactant, it is the rate of oxygen transport to the surface that limits the overall reaction rate. Oxygen concentration over the surface and oxygen coverage of the surface approaches zero and the surface becomes predominantly covered by the partial oxidation species, CO and H in particular. Therefore, lightoff under the fuel-rich conditions is associated with a stepwise switch of the catalyst surface from oxygen covered to CO and hydrogen covered. Appearance of partial oxidation products in the gas mixture after the ‘lightoff’ is consistent with the catalyst being covered by CO and hydrogen, which desorb from the surface into the gas phase. Adsorption of CO and H species to the metal surface is much stronger than that of CO_2 and H_2O molecules. Therefore, at lower temperatures, just after the ‘lightoff’ the rate of CO and H_2 desorption is low compared to the rate of oxygen transport to the catalyst, such that most of these species get oxidized to CO_2 and H_2O before leaving the surface. As the catalyst temperature increases CO and H desorption rates increase, which manifest in increasing process selectivity towards the partial oxidation products CO and H_2.

Lack of oxygen over the catalyst surface provides an additional benefit of limiting formation of metal oxides, which are often more volatile than the reduced metal. It is known, for example, that loss of Pt in the form of PtO_2 is a significant mechanisms for catalyst deactivation under fuel-lean operation. Under fuel-rich conditions, however, volatility of the catalyst is not a significant deactivation mechanism, allowing long catalyst life and broad choice of catalyst materials, without constraints regarding oxide volatility.

The proposed mechanism of fuel-rich ‘lightoff’ is consistent with the results reported by Burch and Loader [26], who observed similar ‘lightoff’ behavior over Pt/Al_2O_3 powder catalyst under diluted fuel-rich mixtures. It is also supported by findings of a recent study by Schmidt and co-workers [25] of alkane oxidation ignition over noble metal catalysts. In this work, a simple surface reaction model was able to closely reproduce experimental data and also suggested a switch from oxygen to CO and hydrogen covered surface at catalyst ignition. Variations in reaction rate due to a step change in surface coverage are also known in literature. For example, such phenomena was well characterized by Ertl [40] for CO oxidation over single crystal Pt and Pd surfaces. They found that the sticking coefficient for CO adsorption on the catalyst was higher over regions of the surface covered by CO than over regions covered by oxygen. In more recent work, where surface reactions were directly monitored by scanning tunneling microscopy [41], it was also found that dissociation probability for an oxygen molecule becomes affected by species chemisorbed in the vicinity. It is likely, therefore, that similar to CO adsorption, catalyst surfaces covered by CO and H species are more active for methane dissociation than surfaces covered by O species. This explains a stepwise increase in methane conversion associated with the catalyst ‘lightoff’ at constant temperature, and higher conversion of methane observed under fuel-rich conditions than under fuel-lean conditions for the same catalyst sample.

6. Conclusions

For Pt, Pd and Rh catalysts greater activity to methane oxidation was found under fuel-rich conditions than under fuel-lean. We attribute this to different intermediate species adsorbed on the catalyst surface. Following lightoff the surface is covered by oxygen when reacting fuel-lean mixtures, while covered by CO and H species when reacting fuel-rich mixtures. Greater activity under fuel-rich conditions provides reduced catalyst lightoff and extinction temperatures for catalytic combustion systems. Absence of adsorbed surface oxygen minimizes catalyst loss through volatilization as precious metal oxide.

It was shown that a fuel-rich catalytic reactor can stabilize lean-premixed combustion downstream of the catalyst, with ultra-low NO_x emissions, and without auto-ignition issues. Catalyst temperature is insensitive to equivalence ratio, allowing wide variations in inlet fuel/air ratio (tolerant to fuel/air unmixedness). Under adiabatic conditions the catalyst remains active at temperatures below 120 °C, allowing operation without a preburner. In addition, the extent of catalytic reaction (heat release) is limited by available oxygen in the fuel-rich mixture, giving a level of reactor robustness that is not possible in fuel-lean catalyst systems using flammable mixtures.

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