

LOW NO_x HYBRID CATALYTIC RADIANT GAS BURNER

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Abstract

An extensive experimental campaign was carried out on a prototype hybrid radiant burner with ultra low emissions based on the novel concept of fuel-rich catalytic + homogeneous flame combustion with interstage heat transfer. Special attention was paid to the impact of two alternative active formulations for the catalytic partial oxidation stage (0.5% Rh and 0.25-0.25% Rh-Pt on γ -Al₂O₃) on the general performance of the burner, and particularly on its NO_x emissions. The hybrid burner was operated with methane in the 4 – 30 kW power range, at varying the feed equivalence ratio ϕ from 2.0 to 3.6. InfraRed thermography was used to simultaneously investigate the catalytic surfaces and the corresponding subsequent diffusion flames. Moreover this work attempts to correlate detailed experimental data on syn-gas compositions at the exit of the CPO reactor with emissions in the exhausts. Experimental evidence of the reduction of both thermal and prompt NO_x formation mechanism is presented.

Introduction

Due to the increasing use of natural gas (NG) to meet the world's energy demand, large research efforts are devoted to the reduction of NO_x emissions and increase of safety and efficiency in NG combustion appliances at both industrial and domestic level [1-3]. Currently, both industrial and utility gas turbine manufacturers prefer lean-premixed combustion technology which has demonstrated the ability to achieve an impressive reduction in NO_x emissions during operation on natural gas [1]. A similar picture is also valid for non-adiabatic (radiant) burners for domestic and industrial applications [2]. As flame temperatures are reduced to achieve low levels of emissions, flame stability and safety issues may arise [1].

Premixed catalytic combustion technology can guarantee the lowest NO_x emissions compared to other combustion options [2,4], but it has not reached a widespread use mainly due to the lack of a single catalyst capable to fulfil all the requirements in terms of high activity, thermal and mechanical stability, long term durability and low cost [4].

Recently we have adapted the concept of fuel-rich catalytic combustion [1,5] proposing a novel staged hybrid catalytic gas burner, with integrated interstage heat removal by IR radiation from the hot catalytic reactor/radiator [6]. A first prototype burner with a structured Rh/Al₂O₃ catalytic partial oxidation (CPO) stage followed by a purely diffusive flame has proved to guarantee significant enhancements with respect to the state-of-the-art fully premixed or blue-flame diffusive gas burners for domestic condensing boilers [6].

In this work we set out to study the impact of two catalytic formulations (namely 0.5 % Rh and 0.25-0.25% Rh-Pt on γ -Al₂O₃) on the main features and NO_x emissions performance of the prototype catalytic hybrid burner in its simplest configuration with a purely diffusive secondary flame. The burner was operated at atmospheric pressure on methane in the 4 – 30 kWth power (P) range, at varying the feed equivalence ratio ϕ from 2.0 to 3.6.

Experimental

Structured catalytic elements were prepared starting from a metallic gauze made of a high temperature FeCrAlloy knitted wire ($d \approx 120 \mu\text{m}$) in the form of flexible cylindrical sockets

[13] (external diameter $D=80\text{mm}$, effective height $H=80\text{mm}$, thickness 2mm , apparent density 0.38 g/cm^2). The substrates were accurately cleaned, oxidized in air at 800°C to start to develop the characteristic superficial protective alumina layer on the alloy, and finally washcoated with 3% La_2O_3 -stabilised $\gamma\text{-Al}_2\text{O}_3$ (SCFa140-L3 Sasol, $140\text{m}^2/\text{g}$.) applied by a dip-coating procedure [6]; the target alumina loading of $\sim 7\%$ wt. was obtained with two deposition cycles followed by calcination in air at 800°C for 3h. SEM observation of the coated FeCrAlloy gauze revealed the presence of a well adhering porous layer on the metallic wire with an average thickness in the range $7\text{-}14\ \mu\text{m}$.

Monometallic Rh catalysts were prepared via incipient wetness impregnation onto washcoated FeCrAlloy gauzes using an aqueous solution of $\text{Rh}(\text{NO}_3)_3$ (Aldrich) to achieve the desired loading of 0.5 %wt. (metallic substrate excluded). After impregnation, the catalysts were dried at 120°C and calcined in air at 550°C . Bimetallic Rh-Pt catalysts were prepared by sequentially impregnating calcined Rh samples (with Rh loading 0.25 %wt.) with a solution of H_2PtCl_6 . The target Rh/Pt weight ratio was 1 and the total nominal metal loading was 0.5 %wt. with respect to the applied alumina layer.

The hybrid catalytic burner under typical operation together with a rendering of its longitudinal section are presented in Figure 1: the fresh gas mixture flowed radially through a distributor, the CPO gauze reactor and then into the flame [6]. The hybrid burner was tested in upward position and secondary air for flame combustion was withdrawn by natural convection from the surroundings. Pure methane and compressed air flows were regulated by two independent mass flow controllers and mixed at atmospheric pressure. Combustion tests were always performed with a fuel rich mixture fed to the burner at an equivalence ratio ϕ variable in the range 2.0 – 3.6 (i.e. above upper flammability limit). The nominal thermal power was varied between 3.8 and 29 kW based on the lower heating value of methane. The resulting gas hourly space velocity (GHSV) at room temperature was comprised between $0.1 - 1.0 \cdot 10^6\ \text{h}^{-1}$, referred to the empty volume of the catalytic mesh, corresponding to a contact time between 0.9 and 10 ms at the reaction temperature.

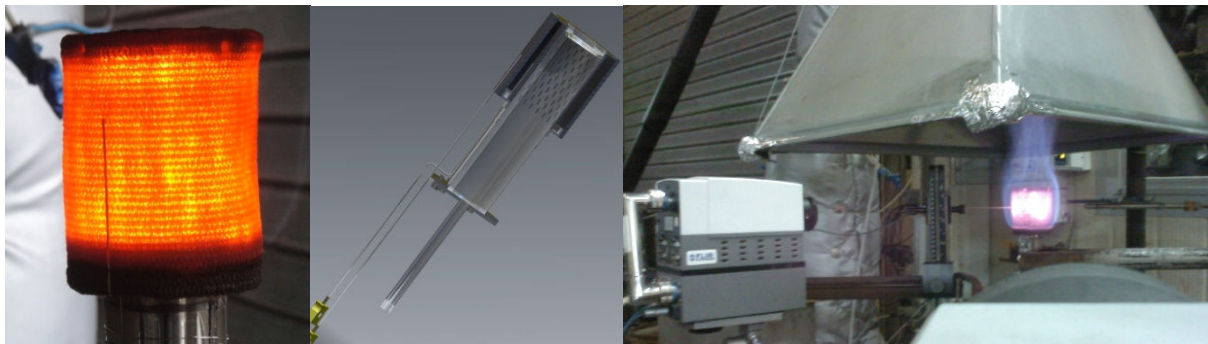


Figure 1. Picture of the catalytic combustion head under typical operation (left), rendering of its longitudinal section (centre), and view of experimental set-up for IR thermography (right).

InfraRed thermography was selected as a fast, not-intrusive, flexible measurement tool to investigate the hybrid burner and to obtain simultaneously the temperature profile on the catalytic surface and an estimation of the flame temperature and structure. Two FLIR thermocameras were employed: a Phoenix with digital acquisition system, and a SC500, respectively with spectral sensitivities in the range $1.5\text{-}5\ \mu\text{m}$ and $7.5\text{-}12\ \mu\text{m}$. Independent thermocouple measurements were preliminary performed to set appropriate emissivity factors, which were checked against literature ranges [14-19]. Further calibration tests were performed for the Phoenix camera using a black body up to 1700 K. In particular, two optical spectral filters centred at 3.4 or $3.9\ \mu\text{m}$ were applied on the Phoenix camera in order to

eliminate flame (gas) emissivity when measuring the surface temperature of the catalyst; a further filter at 4.25 μm was used to estimate CO_2 (flame) temperature [19]. Moreover, the flame images filtered at 3.9 μm allowed us to identify the possible presence of soot formation. All the IR pictures hereafter represent a 5s-average of the images collected at 340 frames/s.

The temperature of the syn-gas emerging from the catalytic stage was also measured with a shielded (Inconel 600, $d=0.5\text{mm}$) K-type thermocouple placed 1 mm downstream from the catalyst surface and parallel to it.

Gas analysis was performed in real time with ABB Advance Optima instruments equipped with ND-IR/-UV, TC and paramagnetic detectors (respectively for CH_4 , CO , CO_2 ; NO , NO_2 ; H_2 ; O_2). The effluent gas from the catalytic partial oxidation stage was sampled with a cooled stainless steel probe in close contact with the surface of the catalytic gauze.

Methane conversion and selectivities to CO and H_2 were calculated according to the following definitions, based on exit dry-gas mol fractions of CH_4 , CO , CO_2 , and H_2 from the CPO reactor:

$$x_{\text{CH}_4} = 100 \cdot \left(1 - \frac{\text{CH}_4^{\text{OUT}}}{\text{CH}_4^{\text{OUT}} + \text{CO}_2^{\text{OUT}} + \text{CO}^{\text{OUT}}} \right)$$

$$S_{\text{CO}} = 100 \cdot \left(\frac{\text{CO}^{\text{OUT}}}{\text{CO}_2^{\text{OUT}} + \text{CO}^{\text{OUT}}} \right)$$

$$S_{\text{H}_2} = \frac{100}{2} \cdot \left(\frac{\text{H}_2^{\text{OUT}}}{\text{CO}_2^{\text{OUT}} + \text{CO}^{\text{OUT}}} \right)$$

Exhaust gases from the burner were collected by a hood and the emissions of CO , NO_x and CH_4 were corrected to 0% O_2 conditions.

Adiabatic flame temperatures were calculated using CHEMKIN 4.1.1 software assuming a stoichiometric flame, based on the measured compositions and temperatures of the effluent gas streams from the CPO stage with both catalytic formulations.

Results and Discussion

IR analysis of the hybrid burner (Fig. 2) showed the presence of an axial-symmetric laminar diffusive flame structure surrounding the hot radiating catalytic reactor, which had a very uniform temperature distribution on the whole outer surface. The flame itself, which appeared blue and had a low-luminosity, was found to be non-sooting, as confirmed by careful inspection of IR images collected at $F=3.9\mu\text{m}$ in the gas phase surrounding the burner (Fig.2 b). Hot gas leaving the combustion head through the catalytic gauze were slightly colder than the catalyst itself. This was also confirmed by the thermocouple measurements [6] and implies that, inside the structured catalytic layer, heat generation occurs through surface oxidation reactions and the flowing gases are only heated by convection. Moving away from the catalytic surface along the radial coordinate we observed an initially flat temperature profile in the gas phase due to the absence of oxidation reactions close to the head: all of the oxygen from primary air was consumed by catalytic oxidation reactions (see next section), and more O_2 from the surrounding air had to diffuse to complete combustion. Thereafter T_{gas} raised to a maximum in correspondence of a symmetric laminar diffusion flame front developed around the burner and above it, which was well captured by CO_2 profiles ($F4.25\mu\text{m}$). However, It should be underlined that temperature profiles in the gas phase were obtained by measuring the characteristic emission of CO_2 at $4.25\mu\text{m}$, therefore they are only qualitative due to varying CO_2 concentration, spatial integration of the emission, flame thickness, presence of an emitting/adsorbing/reflecting surface behind the flame [19] (which was particularly evident for low values of ϕ as in Figure 3 c, i.e. when the catalyst ran hotter).

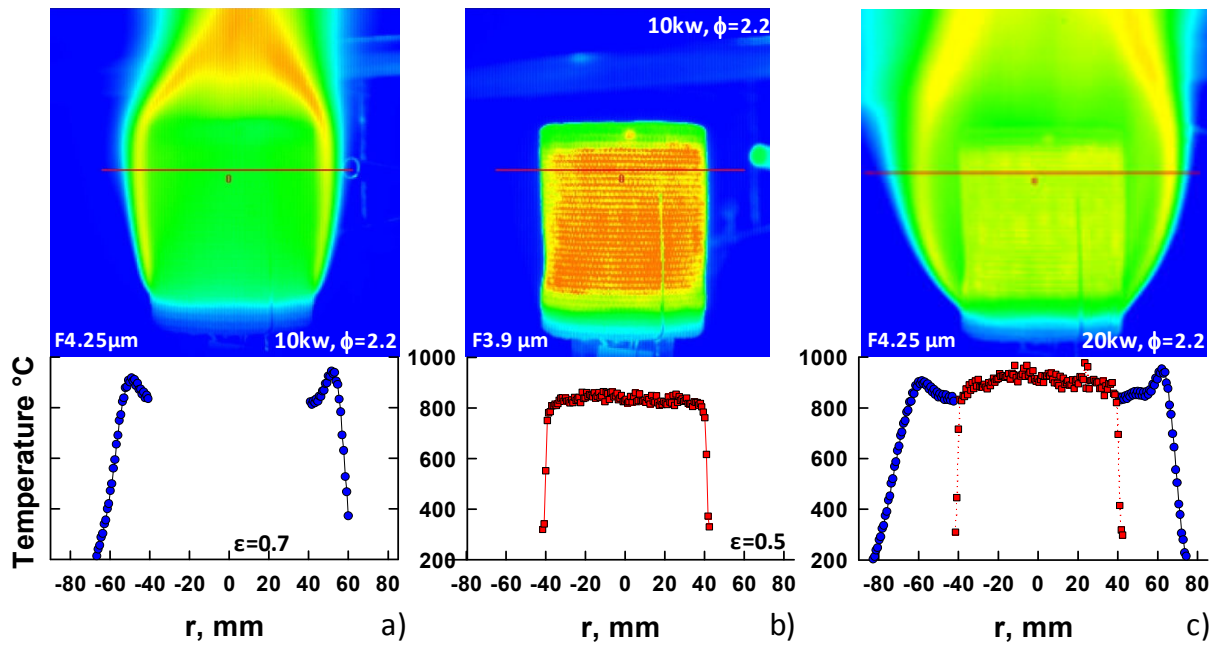


Figure 2. InfraRed images of the flame structure (CO_2) and of the catalytic surface collected at $4.25\mu\text{m}$ and $3.9\mu\text{m}$ respectively, together with the corresponding temperature profile at fixed height along the line shown in figure. Rh catalyst operated at $\phi=2.2$: a) $P=9.6\text{kW}$, $F=4.25\mu\text{m}$; b) $P=9.6\text{kW}$, $F=3.9\mu\text{m}$; c) $P=19.2\text{kW}$, $F=4.25\mu\text{m}$.

The laminar flame envelope expanded at higher input power (and lower ϕ), due to the corresponding higher flow rate and exit velocity of the gas leaving the catalytic head in the radial direction, which pushed the diffusive flame front away from the catalyst. Since the catalyst was hotter at lower values of ϕ , it also preheated the reformed exit gas to a large extent. It is also clear that the flame front extended well above the catalytic head, due to the relatively slow diffusion of oxygen from the surroundings and to poor mixing effectiveness with secondary air achieved by natural convection.

The hybrid catalytic burner performs a staged combustion, and is characterized by interstage heat transfer by IR radiation from the hot catalytic head to a heat sink. By this way the peak temperature reached at the diffusion flame front can be strongly reduced. This is shown in Figure 4 a-b which reports the temperatures measured on the outer surface of the two catalytic gauzes as a function of ϕ and for 3 nominal power levels, together with the corresponding adiabatic flame temperatures calculated from the measured composition of the syn-gas leaving the catalytic stage. For both catalysts the outer surface temperatures were comprised in the range 650°C - 1050°C , strongly increasing with decreasing ϕ , due to a larger availability of the limiting reactant (oxygen) for the heterogeneous oxidation reactions. Higher temperatures were also measured at constant ϕ for a higher nominal power (i.e. flow rate) to the burner: this is a well recognized feature of non-adiabatic CPO reactors, because heat loss does not scale with flow rate as long as the contact times are adequately long to maintain full O_2 conversion [9].

From Figure 3 it appears that the bimetallic catalyst always ran $50\text{-}100^\circ\text{C}$ hotter than its monometallic Rh counterpart at any fixed P level, which also precluded to explore very low ϕ values in order to prevent catalyst overheating and deactivation. It was already reported that substitution of half of the Rh loading with same weight amount of Pt entails a significant increase in the operating temperatures of methane CPO monoliths, since reactions leading to total oxidation products become more important on Pt [12]. In fact the higher syn-gas yield on Rh catalyst is strictly associated to its higher activity for the endothermic methane steam

reforming reaction whose contribution is significant even at very short contact times [8,10], and strongly non-adiabatic conditions [6,11].

As shown in the upper part of Fig. 3a,b, the adiabatic flame temperature of the syn-gas follows an opposite trend with respect to the catalyst temperature, progressively decreasing for lower ϕ values, as a consequence of the larger quantity of heat transferred by radiation from the hotter catalytic surfaces. However, at fixed ϕ , the adiabatic flame temperature increases with the nominal input power due to a reduction in the percentage of heat loss from the CPO reactor. In fact, the fraction of thermal power emitted by the hot radiating catalyst decreased progressively for higher values of the input power, although its absolute value increased due to higher surface temperatures [6].

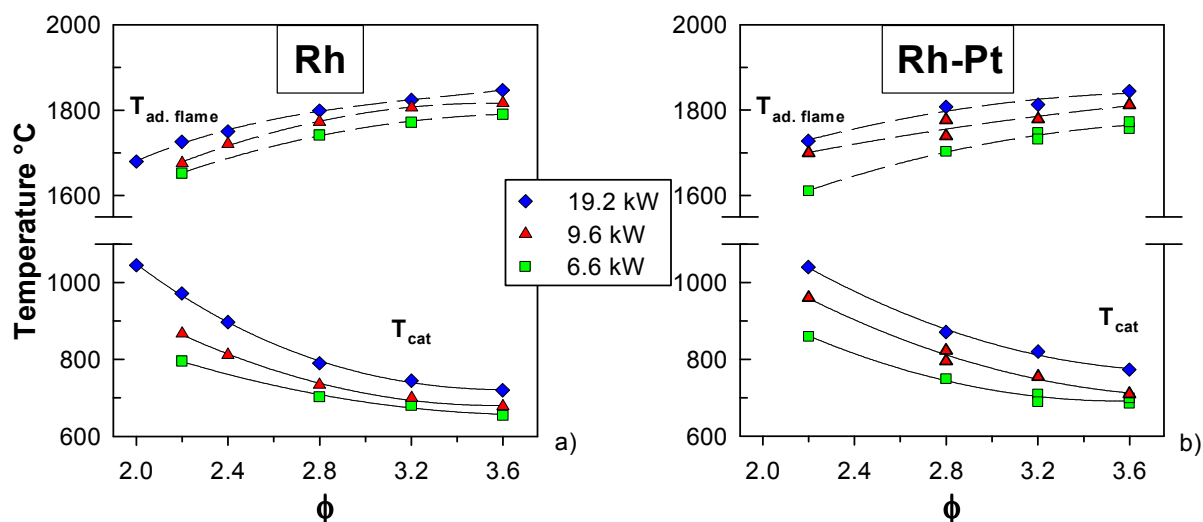


Figure 3. Temperature of the outer catalytic surface and corresponding adiabatic flame temperature of the emerging syn-gas for Rh (a) and Rh-Pt (b) catalysts as a function of ϕ at different power levels.

Catalytic Partial Oxidation Stage

Figure 4a-e compare the catalytic activities of supported Rh and Rh-Pt catalysts during the CPO of methane as a function of the feed equivalence ratio ϕ for several Power levels. Gas analysis at the exit of the CPO reactor confirmed that O_2 conversion was always complete on both catalysts for all conditions explored [6, 8-12], whereas no sign of NO_x formation could be found. Methane conversion and selectivities to CO and H_2 followed the general trends predicted by thermodynamic equilibrium calculations (solid lines in Fig.4) under adiabatic conditions, departing from them in a measure depending on both the active phase composition and the specific input power level (P).

Monometallic Rh catalyst showed the best performance in terms of methane conversion, which increased steadily with decreasing ϕ , respectively exceeding 90% for $\phi \leq 3.0$ and 99% for $\phi \leq 2.2$, whereas it was almost unaffected by the value of P in the range explored. Partial substitution of Rh with Pt entailed a reduction in fuel conversion by roughly 5 percentage points for values of ϕ down to 2.4, leaving about 2-3% of unconverted methane also at $\phi = 2.2$. Moreover Rh catalyst showed a higher selectivity to both CO and H_2 , which is particularly evident when comparing the relevant plots at lower values of power. However, similar selectivities to syn-gas were measured on the two catalysts at the highest values of P, as a consequence of the higher associated operating temperatures (Fig. 3) leading to a closer approach to thermodynamic equilibrium values.

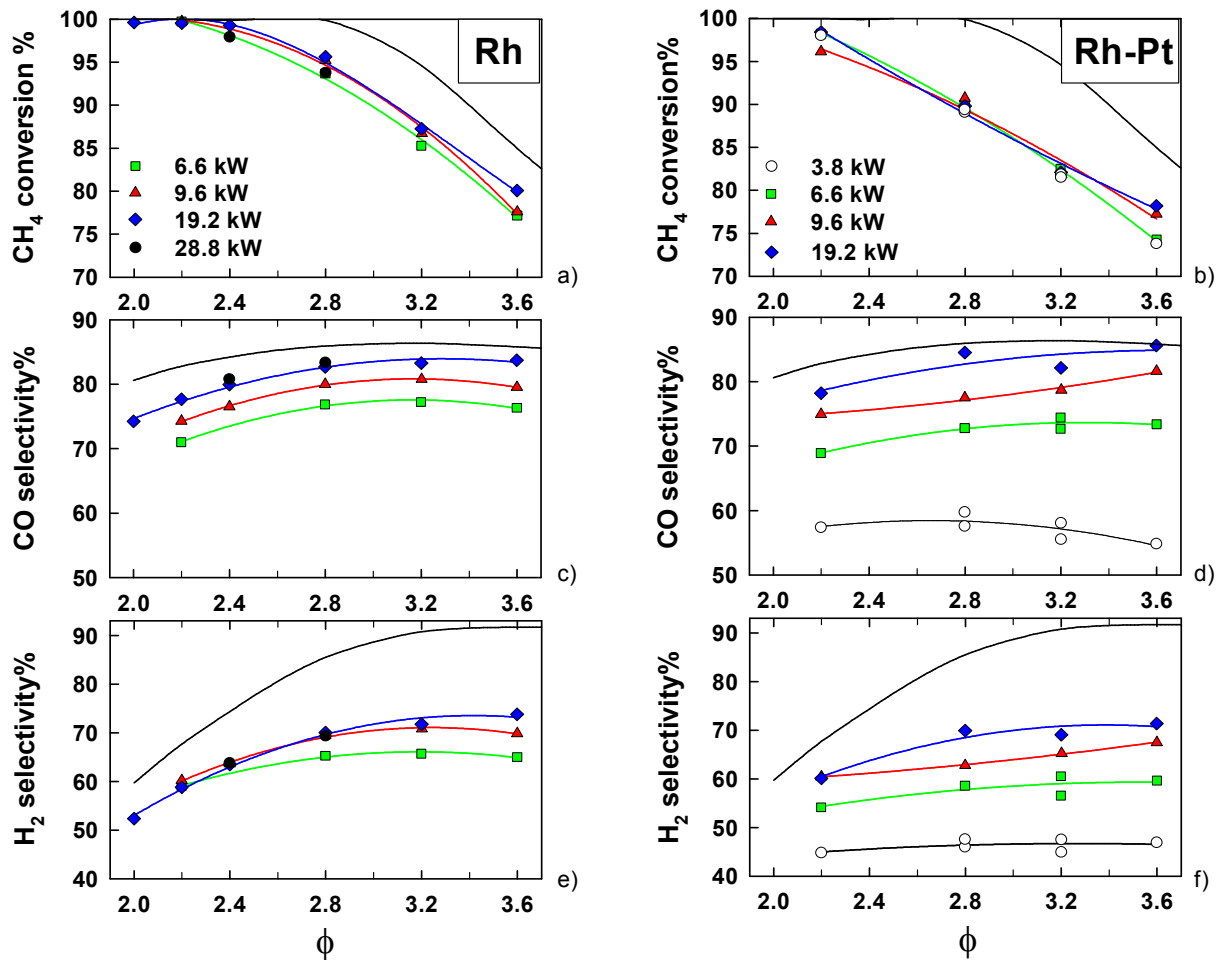


Figure 4. Methane conversion (a, b), CO (c, d) and H₂ (e, f) selectivities as a function of ϕ at several nominal power levels. Rh (left panels) and Rh-Pt (right panel). Solid lines represent thermodynamic (p, H=constant) equilibrium values.

CO and CH₄ emissions

Irrespective of catalyst formulation, CO emissions from the hybrid burner were always ≤ 60 ppm (corrected @0% O₂), and resulted weakly affected by ϕ only at low-mid input Power levels, where they slightly decreased if more primary air was fed to the catalyst. At the same time, unburned CO decreased strongly at higher Power levels (6-7 ppm at 19.2kW), suggesting that most of the emissions were due to local quenching effects possible at low flow rates, when the diffusive laminar flame front was placed very close to the catalytic combustion head. Moreover CH₄ emissions in the exhaust were always below the detection limit (10ppm) with both catalysts and for the whole range of conditions explored, confirming our previously reported results [6]. Syn-gases with dominant carbon monoxide and hydrogen fractions present a much wider ignition range than those of conventional hydrocarbon fuels of natural gas [20]. In the hybrid burner the operational range for homogeneous combustion is further expanded by the high preheating of the fuel produced in the catalytic stage and by its high H₂ content, which facilitates the oxidation of other organic fuel fractions. Both circumstances effectively lower the probability of unburned gas eddies of improper mixing, resulting in low emissions of unburned CO and methane, even in systems with poor mixing judged by the standard of conventional design [20].

NO_x emissions

Since no evidence of NO_x formation could be detected at the exit of the catalytic partial oxidation stage, NO_x emissions from the hybrid burner are only due to the homogeneous flame combustion stage: in the simple current configuration, syn-gases emerging from the catalytic gauze were burned under purely diffusive and laminar conditions. Figure 5a,b reports the emissions of NO_x (@0% O₂) as a function of ϕ at different power levels for the two catalytic formulations tested. In both cases NO_x concentrations in the exhaust decreased almost linearly with decreasing ϕ , following the same trend of the adiabatic flame temperature of the syn-gas, which was progressively lowered by the increase of interstage heat removal through radiation. Moreover, along with the general increase in the flame temperature levels with the nominal power, also NO_x emissions increased, ranging from 10 to 60 ppm and from 10 to 80 ppm for Rh and Rh-Pt catalysts respectively. In fact, at any fixed power level, monometallic Rh catalyst guaranteed a significant reduction in NO_x emissions over its bimetallic counterpart.

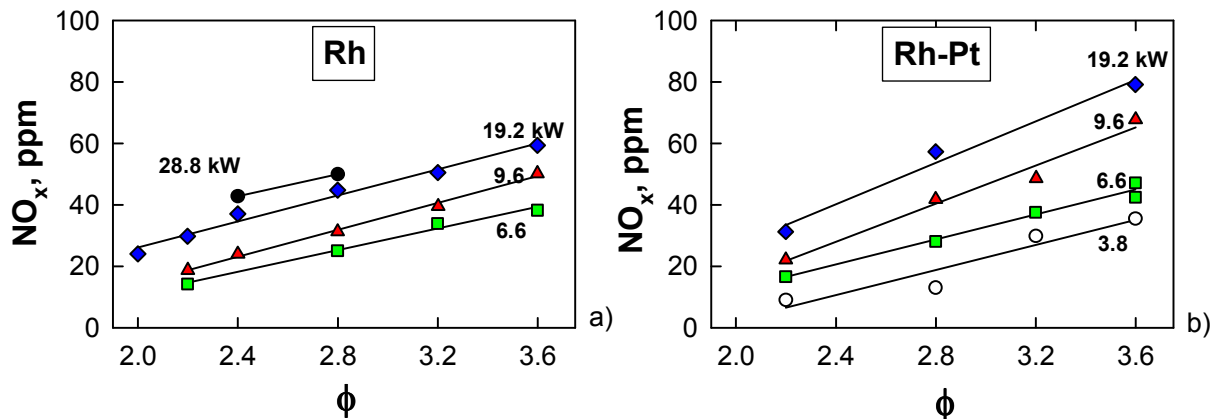


Figure 5. Total NO_x emissions corrected @0% O₂ from hybrid burner with Rh (a) and Rh-Pt (b) catalyst as a function of ϕ at different power levels.

As a general figure, the emissions of NO measured at the exhaust of two commercial burners, a fully premixed lean surface stabilized device and a blue-diffusive turbulent flame one, ranged respectively between 20 to 60 ppm and 80 to 120 ppm, when operated with their optimal excess of air between 20 and 30% [6]. It came out that both prototypes of the hybrid catalytic burner were able to outperform state-of-the-art premixed burner in terms of NO_x emissions for ϕ values below 3 (Rh) and 2.8 (Rh-Pt), while a maximum of 40-50% reduction in NO_x was achieved with the monometallic Rh-based catalyst operated at the lowest values of ϕ . This result becomes more impressive considering the purely diffusive and laminar nature of the secondary flame under the current burner configuration.

Previous studies on syn-gas combustion in non premixed flames reported that the contributions of thermal and prompt mechanisms to total NO_x are comparable while that of N₂O-intermediate and NNH mechanisms were found to be relatively small and negligible [21 and ref. therein]. In line with those findings, we showed that the strong NO_x reduction achieved by the hybrid burner with integrated heat removal from the catalytic head is largely due to the reduction of the peak flame temperatures responsible for thermal NO_x formation. However, NO_x formation through the prompt mechanism is less affected by temperature due to the relatively low activation energy of the initiation reaction step involving CH radical ($\text{CH} + \text{N}_2 \leftrightarrow \text{HCN} + \text{N}$) [20,21]. In order to separate the thermal and chemical effects, the NO_x mole fractions in the exhaust from the two catalytic burners are presented in Figure 6a as a function of the stoichiometric adiabatic flame temperature of the syn-gas from the CPO stage

calculated from measured compositions and temperatures. When plotted against the adiabatic flame temperature, all of the scattered emission data reported in Fig. 5 collapse in single curves for each catalyst formulation, showing a relatively weak exponential growth with T_{ad} , suggesting a minor role played under such conditions by thermal NO_x with respect to prompt formation mechanism.

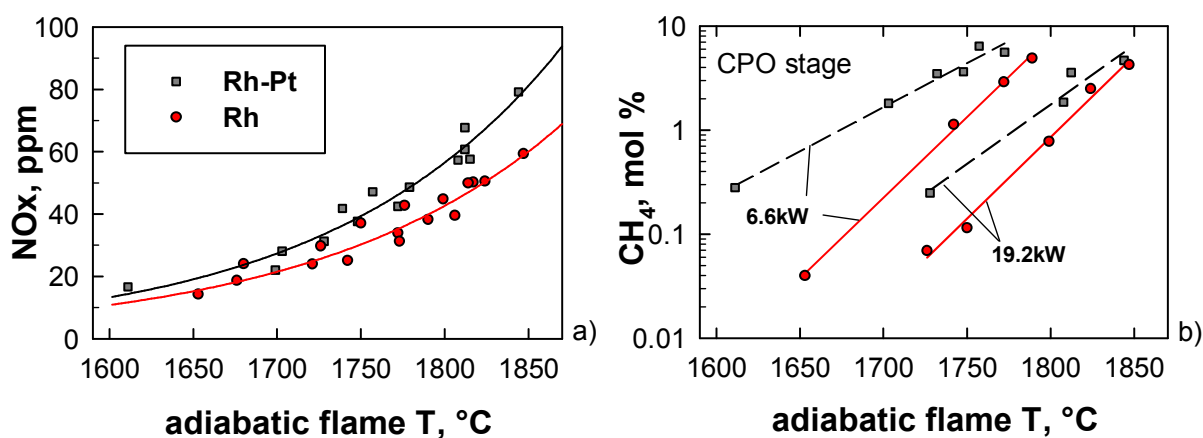


Figure 6. a) Total NO_x emissions corrected @0% O_2 produced by the hybrid burner with Rh and Rh-Pt catalysts as a function of the adiabatic flame temperature of the syn-gas produced. b) Comparison of the residual methane mol fractions in the syn-gas from the two catalysts for two nominal power levels.

For the same adiabatic flame temperature of the syn-gas, monometallic Rh catalyst constantly guaranteed a further 20-25% NO_x reduction with respect to its bimetallic counterpart. In order to explain this behaviour Figure 6b compares the residual CH_4 mole fractions in the syn-gas produced on each of the two catalysts as a function of the adiabatic flame temperature at two power levels. Since a lower fuel conversion in the CPO stage entails an increase in the adiabatic temperature of the subsequent flame, it follows that methane concentration in syn-gas increases progressively along with T_{ad} . From Figure 6a,b it appears that the superior performance of Rh catalyst in terms of lower unconverted methane reflects in a lower formation of prompt NO_x in the flame. In fact it was demonstrated [21] that the presence of relatively small amounts of methane in CO-H_2 mixtures increases the formation of acetylene considerably, which causes a significant increase in CH concentration and thereby in prompt NO_x . A higher residual methane concentration in the syn-gas mixture might also adversely affect soot emissions as a consequence of a predicted increase in acetylene concentration (soot precursor) at high temperature in the flame front [21]. However, non-sooting flames were observed to surround each of the two catalysts. In fact, the large concentration of diluents ($\text{N}_2, \text{H}_2\text{O}, \text{CO}_2$) in the syn-gas fuel prepared by the CPO stage also entailed a beneficial effect for further prompt NO_x , as well as soot, suppression. H_2O , and to a lower extent CO_2 , were reported to have a chemical effect that, for the same peak flame temperature, reduces the concentrations of CH and C_2H_2 [22,23].

Conclusions

Monometallic Rh and bimetallic Rh-Pt on γ -alumina catalysts were anchored onto structured substrates made of a FeCrAlloy knitted wire gauze and tested in a radial flow radiant hybrid burner operated with a fuel-rich methane-air feed and a purely diffusive secondary flame. Both catalysts were able to steadily convert methane with high fuel conversion and selectivities to H_2 and CO under strongly non-adiabatic conditions. The higher (reforming)

activity of Rh determined a higher conversion to syn-gas on the monometallic catalyst, whereas the partial substitution with Pt slightly favoured total oxidation products, therefore sustaining higher surface temperatures (and radiative heat transfer) for the same value of the equivalence ratio ϕ . Indeed, it was possible to finely control the maximum temperature of the catalysts by simply acting on ϕ . Moreover, the adiabatic flame temperature of the produced syn-gas was significantly reduced and followed an opposite trend with respect to the temperature of the catalyst. The hot, diluted, and highly reactive syn-gas from the CPO stage was finally burned in a laminar diffusive flame, which was found to be non-sooting and to produce very low emissions of CO and CH₄, even in a systems with poor mixing. Regarding NO_x emissions, the contribution from thermal formation mechanism was strongly limited due to the significant reduction of the peak flame temperature. Prompt NO_x were also limited due to the high dilution of the syn-gas, which contained low amounts of un-reacted hydrocarbons and high concentrations of H₂O and CO₂. It came out that the prototype hybrid catalytic burner was able to outperform state-of-the-art lean premixed burners in terms of NO_x emissions with as much as 50% reduction achieved with the monometallic Rh catalyst operated at the lowest values of ϕ . For the same adiabatic flame temperature of the syn-gas, the monometallic Rh catalyst always guaranteed a 20-25% NO_x reduction with respect to its bimetallic counterpart, because of a lower contribution from prompt NO_x formation mechanism due to the lower concentration of residual methane in the syn-gas.

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