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CO, H_2 or C_3H_8 assisted catalytic combustion of methane over supported $LaMnO_3$ monoliths

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Abstract

The effect of the addition of a second fuel such as CO, C_3H_8 or H_2 on the catalytic combustion of methane was investigated over ceramic monoliths coated with $LaMnO_3$/La-γAl_2O_3 catalyst. Results of autothermal ignition of different binary fuel mixtures characterised by the same overall heating value show that the presence of a more reactive compound reduces the minimum pre-heating temperature necessary to burn methane. The effect is more pronounced for the addition of CO and very similar for C_3H_8 and H_2. Order of reactivity of the different fuels established in isothermal activity measurements was: $CO > H_2 \geq C_3H_8 > CH_4$. Under autothermal conditions, nearly complete methane conversion is obtained with catalyst temperatures around 800 °C mainly through heterogeneous reactions, with about 60–70 ppm of unburned CH_4 when pure methane or CO/CH_4 mixtures are used. For H_2/CH_4 and C_3H_8/CH_4 mixtures, emissions of unburned methane are lower, probably due to the proceeding of CH_4 homogeneous oxidation promoted by H and OH radicals generated by propane and hydrogen pyrolysis at such relatively high temperatures.

Finally, a steady state multiplicity is found by decreasing the pre-heating temperature from the ignited state. This occurrence can be successfully employed to pilot the catalytic ignition of methane at temperatures close to compressor discharge or easily achieved in regenerative burners.

Keywords: Supported perovskite; Catalytic combustion; Monolith catalysts; CH_4, CO, H_2, C_3H_8 oxidation kinetics; Assisted methane combustion

1. Introduction

Catalytic combustion is generally accepted as one of the environmentally most preferred alternative for heat and power generation from fossil fuels, allowing to efficiently burn in concentrations outside flammability limits, at temperatures lower than in flame combustion and without undesired by-products, such as UHC, CO, NO_x [1–4]. Interesting applications of such technology have been proposed both at domestic scale (radiant catalytic heaters, camping lamps, cookers) [4,5], and for industrial processes (gas turbines, radiant burners, fluidised bed catalytic combustors, high temperature ovens for endothermic reactions, i.e. steam reforming) [2–4,6].

So far most of the research activity in the field of catalytic combustion for energy production has focused on the use of methane, mainly for its nature of clean fuel, largely available world-wide. Nevertheless, methane is also the most stable, difficult to oxidise hydrocarbon: catalytic ignition occurs at relatively high

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temperatures [7] even on the most active and expensive PdO-based catalysts.

Mixing CH_4 with CO, H_2 or light hydrocarbons, might be advantageous due to the higher reactivity of such compounds which could facilitate start-up [7,8] and/or stabilise the catalytic reaction without the need of further pre-heating or piloting, as proposed in patent literature for gas turbines and micro-turbines [8]. Indeed, catalytic oxidation of a highly reactive fuel could be used to sustain the combustion of the main methane feed instead of an external diffusion-flame preburner, which is usually employed to extend the operating window of catalytic combustors, but accounts for the largest part of polluting emissions [1].

Our recent studies on the dispersion of $LaMnO_3$ perovskite onto high surface area refractory oxides (La/γ-Al_2O_3, MgO and ZrO_2) [9–12] have shown that it is possible to obtain promising monolithic catalysts for premixed methane combustion, characterised by an elevated specific activity and a thermal stability markedly increased with respect to the bulk perovskite. Such supported catalysts might be even more valuable when the fuel comprises also H_2, CO and light hydrocarbons, as in the case of gasified biomass [13–15], syngas and industrial residual gas [16]: indeed this class of cheap catalysts could fill the excessive gap of activity existing between noble metals and hexaaluminates [13,14], replacing them without renouncing to high catalytic performances and/or thermal stability and durability at temperatures up to 1100 °C.

In fact, high concentration of CO were observed in the effluent from a catalytic combustor fuelled by gasified biomass [15,17], whenever the exit temperature from the catalytic section (1 PdO + 2 Mn-substituted hexaaluminate monoliths) was not high enough (>1000 °C) to sustain complete homogeneous oxidation of the CH_4 fraction. Such phenomenon has to be attributed to the well documented drop of activity of PdO-based catalysts associated to the thermal reduction to metallic Pd at temperatures around 700–800 °C, and to the very low activity of following hexaaluminate monoliths [17]. On the other hand, perovskite-based catalysts are remarkably active towards methane oxidation in a wide temperature range [10], making possible to obtain complete heterogeneous conversion within a larger operating window.

Aim of this work is to study the characteristics of the CO, H_2 or C_3H_8 assisted catalytic combustion of lean methane air mixtures on monoliths wash-coated with La/γ-Al_2O_3 impregnated with $LaMnO_3$, checking their performances through the reproduction on a lab scale of autothermal combustion conditions typical of premixed, fully catalytic burners.

2. Experimental

2.1. Catalyst preparation

Commercial cordierite monoliths (Corning) with square-shaped channels and a cell density of 400 cpsi are wash-coated with a γ-Al_2O_3 layer through a repeated dipping procedure [9]. After wash-coat stabilisation with La_2O_3 (7% w/w), the $LaMnO_3$ active phase is dispersed on the monoliths (30% w/w with respect to the wash-coat) by a deposition–precipitation method, as already reported in [9]. Catalytic monoliths are finally calcined at 800 °C in air for 3 h.

2.2. Isothermal catalytic activity measurements

Kinetic tests on the catalytic oxidation of the various fuels are carried out in electrically heated quartz down flow reactor, already described in [10]. The external and central channels of the monolithic reactor (5 × 5 channels, $L = 5.9$ cm) are blocked at both ends with ceramic wool leaving only eight free channels on the cross-section. The central channel is used to measure the monolith temperature with three equally spaced K-type thermocouples; an additional thermocouple measures the temperature of inlet gas 1 cm upstream of the catalyst. The narrowing of the reactor section in pre- and post-catalytic zone limits the occurrence of homogeneous reactions. Reactor configuration, coupled with very lean inlet mixtures, allows to keep temperature gradients in the axial direction always within ±2.5 °C. Air, N_2, CH_4, CO, H_2 or C_3H_8 flowing from cylinders are independently regulated by Brooks 5850 mass flow controllers, premixed at atmospheric pressure and fed to the reactor at $F/W = 66\,000$ N cm^3/(g h), unless otherwise stated. On-line continuous analysis of reactants and products is performed (after water removal through a condenser and a $CaCl_2$ trap) using a Hartmann and Braun Advance Optima apparatus equipped with independent NDIR detectors

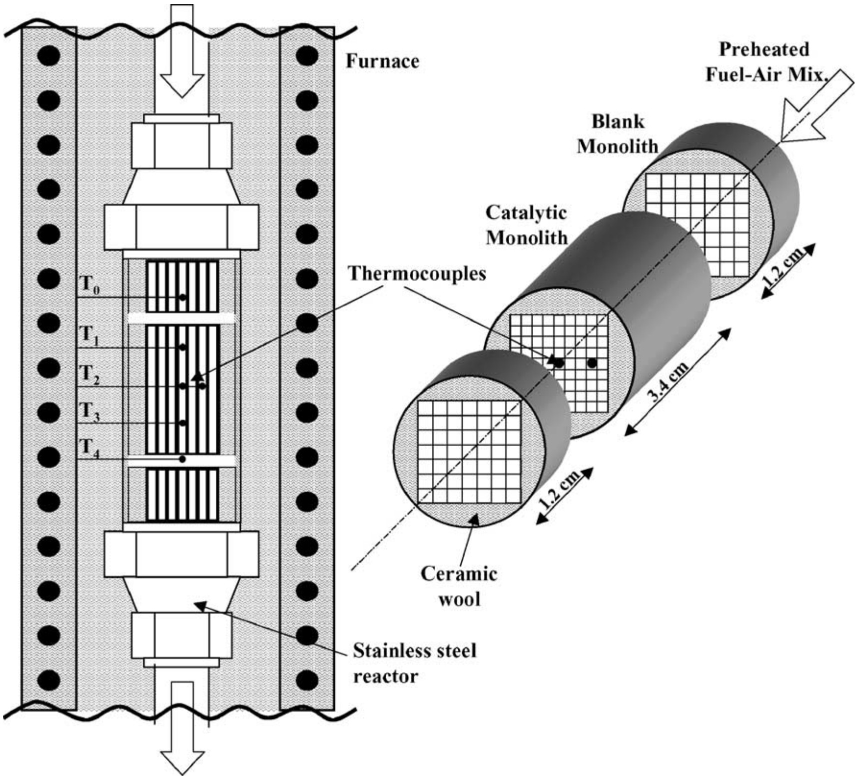

Fig. 1. Schematic of the experimental set-up for autothermal catalytic combustion experiments over monolithic reactors.

(URAS 14) for CH_4, CO, CO_2, NO and a TC detector (CALDOS 17) for H_2 with automatic correction for the interference from all other measured species.

2.3. Autothermal catalytic combustion

Combustion experiments are carried out in a 2.54 cm OD stainless steel downflow reactor, placed inside a three-zone high precision electrical tubular furnace. Fig. 1 depicts a schematic of the reaction zone constituted by a 3.4 cm long catalytic monolith (9×9 channels) insulated and held in position inside the SS tube by means of ceramic wool. Two blank cordierite monoliths (200 cpsi, $L = 1.2$ cm) are placed 0.5 cm before and behind the catalyst in order to achieve a uniform flow distribution and to reduce heat losses due to radiation from both ends. The central channel of the catalyst is blocked for wall temperature measurement with K-type thermocouples ($d = 0.5$ mm), two of which entering from the top and two from the bottom of the monolith. The axial positions are determined by comparing gradations on the thermocouples against a length scale, with an accuracy estimated within ±1 mm: from catalyst inlet section T_1: 0.6 cm; T_2: 1.7 cm; T_3: 2.7 cm; T_4: 3.4 cm, in contact with outer face (Fig. 1). Additional thermocouples are located both upstream of the catalyst (T_0: -1 cm, inside the dummy monolith) and in the middle of a side channel, in order to evaluate inlet gas temperature and radial heat transfer effects, respectively. All combustion experiments are conducted at atmospheric pressure with fully premixed, lean fuel/air mixtures (always below composite Lower Flammability Limit at ambient temperature), and total flow rate fixed at 48 or 60 N l/h (GHSV $= 16\,000/20\,000\ h^{-1}$, based on monolith empty volume). Spatio-temporal temperature patterns in the reactor and concentrations of exit products are simultaneously acquired and recorded on a PC.

Transient experiments are carried out by adding stepwise the fuel–air mixture on the pre-heated catalyst; oven temperature is either kept constant or varied at fixed rate (3 °C/min). Blank tests have been performed to evaluate the actual pre-heating temperature progression of the catalytic reactor.

In autothermal experiments, maximum monolith temperatures are limited by radiative and conductive heat exchange from outer hot catalytic surfaces towards colder oven walls: such phenomenon is significant because of the relatively high external surface to volume ratio characteristic of our lab-scale monolithic reactors [10].

3. Results and discussion

3.1. Fuel oxidation activity

Fig. 2 reports the conversion data for CH_4, C_3H_8, H_2 and CO obtained in single component experiments as a function of the reaction temperature; in these tests, the inlet concentrations of each fuel were chosen in order to obtain similar heating values.

In agreement with literature data on bulk perovskites [16], the reactivity order is $CO > H_2 \geq C_3H_8 > CH_4$; complete selectivity to CO_2 and H_2O is observed in each case. Values of T_{10}, T_{50} and T_{90} (temperature for 10, 50 and 90% conversion) reported in Table 1 indicate that the oxidation of CO occurs in a temperature range roughly 200 °C below that of CH_4 and 100 °C below H_2 and C_3H_8. Apparent activation energies, calculated assuming isothermal plug flow conditions and 1^{st} order rate expression for all fuels, rise following the reactivity scale, being, respectively, 13, 15, 18 and 19 kcal/mol (Table 1). These values are in good agreement with those reported for the oxidation of CO, H_2 and C_3H_8 on bulk transition metal perovskites and hexaaluminates [16,18–20], while the slightly lower activation energy obtained for methane combustion has been attributed to the presence of residual MnO_x clusters or superficial Mn–Al spinel structures over the fresh catalyst pre-treated at 800 °C [9].

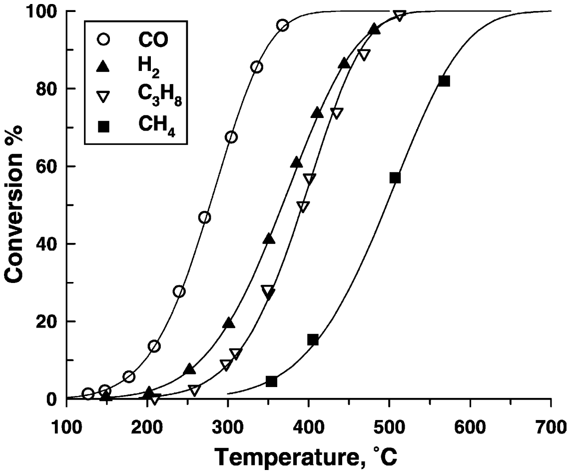

Fig. 2. Conversion plots for different fuels over a catalytic monolith based on supported $LaMnO_3$. Inlet conditions: CO = 1% (or H_2 = 1%, or C_3H_8 = 0.14%, or CH_4 = 0.4%), O_2 = 10%, bal. N_2.

Dispersion over the high surface area La/γ-Al_2O_3 layer enhances the overall oxidation activity of the supported $LaMnO_3$ catalyst with respect to the pure perovskites [9,10,18–20], especially when considering that the actual loading of active phase is limited to only 30% w/w of the wash-coat. In order to give an overall picture of the catalytic performances, Table 1 reports the values of 1^{st} order kinetic constants (k_w) calculated at 350 °C for each fuel over the present catalyst as compared to those extrapolated form activity data on various bulk $LaMnO_3$ catalysts and also on two Mn-substituted hexaaluminates tested by other authors under similar experimental conditions [13,16]. Despite the large difference in calcination temperatures, a common feature appears evident: over the monolith coated with supported $LaMnO_3$ methane oxidation activity is increased by a factor that varies from 18 to 53; at the same time, the difference in reactivity between CO and CH_4 is reduced by an order of magnitude.

Moreover, after prolonged and repeated ageing at temperatures as high as 1100 °C under reaction, the activity of this catalyst for CH_4 combustion decreases to a constant and stable value which is four times lower than the initial one [10], but still much larger than those attained by corresponding (fresh) perovskites and hexaaluminates.

3.2. Assisted autothermal combustion

It is well documented that the catalytic ignition of methane is a kinetically controlled phenomenon [6,7,10,22]: the minimum pre-heating temperature

Table 1
Summary of the performance of the supported $LaMnO_3$ catalyst in the deep oxidation of pure fuels with 10% O_2 (balance N_2)[a]

Fuel	ΔH_{comb} (kcal/mol)	Molar fraction (%)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	E_a (kcal/mol)	k_w at 350 °C (N l/g h)			
							Present work	Bulk $LaMnO_3$	BMA[b]	SLMA[c]
CO	67.6	1.0	197	278	347	13.0	337	508[d]	112	191
H_2	57.8	1.0	266	368	456	14.6	69.8	19.5[e]	2.97	28.0
C_3H_8	488	0.14	305	392	464	17.7	41.1	17.0[f]	–	–
CH_4	192	0.40	389	497	587	19.0	6.33	0.36[g]	0.12	0.26

[a] E_a and k_w calculated under the assumption of isothermal plug flow reactor and 1st order kinetics with respect to the fuel (0th order O_2). k_w values refer to total weight of wash-coat layer.

[b] $BaMnAl_{11}O_{19}$ from Ref. [13]; calcined at 1300 °C.

[c] $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ from Ref. [16]; calcined at 1300 °C.

[d] Adapted from Ref. [19]; catalyst calcined at 800 °C.

[e] Adapted from Ref. [20]; catalyst calcined at 750 °C.

[f] $La_{0.68}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ from Ref. [18]; calcined at 650 °C.

[g] Adapted from Ref. [9]; catalyst calcined at 800 °C.

required for light-off of the reaction (T_{ig}) is weakly affected by space velocity [12] and therefore usually employed as a direct measure of catalyst oxidation activity. In order to check the feasibility of assisting catalytic methane combustion with CO, H_2 and C_3H_8, the variation of minimum ignition temperatures can be used to quantify the enhancement of reactivity with respect to a standard case of pure CH_4 (3% v/v in air). To this aim binary fuel mixtures were prepared with the same overall heating value (1 kJ/N l), i.e. substituting progressively larger fractions of CH_4 with equivalent quantities in terms of combustion heat of the auxiliary fuel (ratio of molar ΔH_{comb}:$CH_4/CO = 2.84$; $CH_4/H_2 = 3.32$; $CH_4/C_3H_8 = 0.39$). In particular, the light-off (ignition) temperature is herein defined as the minimum external pre-heating level for which steady state fuel conversion reaches 90%: for screening purposes, it was evaluated under dynamic conditions by slowly raising the oven temperature while feeding the fuel–air mix to the monolith. Parts a and b of Fig. 3 present the typical evolution of temporary catalyst temperatures and exit conversions as obtained in the case of a CH_4/CO fuel mixture. Light-off temperature is assigned at the point where the 1st derivative of catalyst temporary temperature (and fuel conversion) starts to diverge from the corresponding derivative relevant to blank heating experiments (Fig. 3c). The accuracy of this measure was verified to fall within ±5 °C with respect to steady state ignition temperatures obtained with several experiments at fixed pre-heating levels.

Fig. 4 summarises the results obtained for the auxiliary fuels at different substitution levels. The supported $LaMnO_3$ monolith is able to ignite the reference 3% v/v methane/air mixture at pre-heating temperature of 450 °C, showing a gain of roughly 35 °C with respect to the results previously reported for the same catalyst in a different experimental rig [10]. This improvement has to be mainly attributed to the higher partial pressure of oxygen (air vs. O_2 10% v/v), and to the decrease of heat losses from the catalytic session, which is characterised by a more favourable S/V ratio.

Regarding binary fuel mixtures, in each case the partial substitution of methane with a more reactive compound determines a progressive reduction in the values of pre-heating temperature required for ignition. In agreement with the reactivity order obtained on the perovskite-based catalyst under isothermal conditions, CO is the most effective in lowering the pre-heating temperature, reducing T_{ig} by 65 and 110 °C, respectively, for substitution levels of 25 and 50% of the methane feed. On the other hand, comparable CH_4/H_2 and CH_4/C_3H_8 mixtures require higher pre-heating temperatures, with a slight but still appreciable benefit for hydrogen, accordingly to its faster measured heterogeneous oxidation rate.

As clearly shown in Fig. 3b, ignition of CH_4/CO mix proceeds in two separate steps due to the large difference of reactivity between CO and CH_4: conversion of CO jumps to 100% as soon as the fuel mix is added to the catalyst at 350 °C, while methane requires further external pre-heating to burn completely, and its

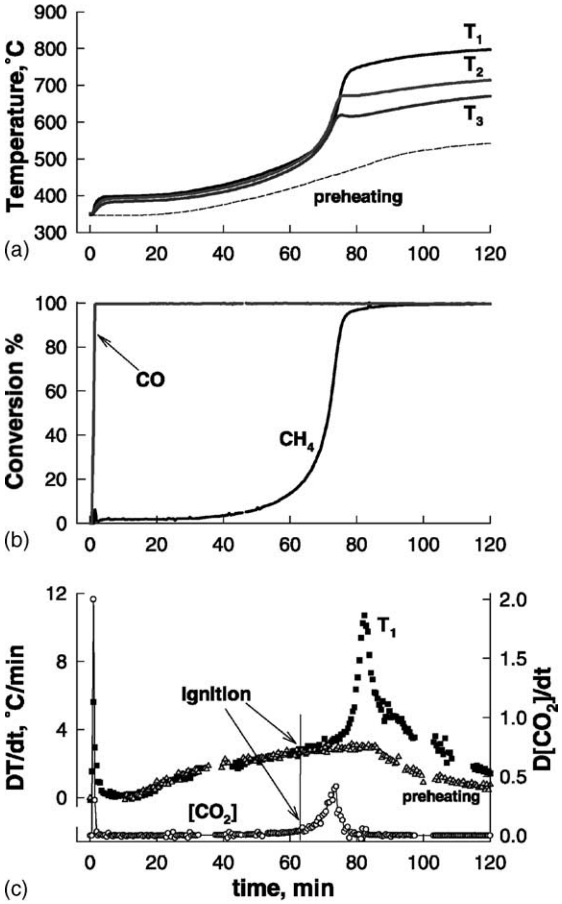

Fig. 3. Typical dynamic ignition experiments showing: (a) temperature profiles, (b) exit fuel conversions and (c) their 1st temporal derivatives in comparison with that of a blank heating experiment. Fuel mix: CH_4 2.6% + CO 1.1% in air; GHSV = 16 000 h^{-1}.

ignition remains the limiting factor. In this case, the reduction in the value of the pre-heating temperature for light-off essentially corresponds to the increment of temperature measured on the catalyst (Fig. 3a) due to the heat released by the heterogeneous oxidation of CO. However, it should be noticed that because of heat losses from the catalytic monolith, the measured temperatures are always below the theoretical adiabatic values calculated from fuel consumption.

Curves in Fig. 4 obtained substituting H_2 and C_3H_8 for methane show different slopes and higher ignition temperatures with respect to the corresponding curve for CO. Due to the lower reactivity of hydrogen and propane, at the same temperature they are not completely converted and thus only part of their heat of combustion is effectively employed to assist the ignition of methane.

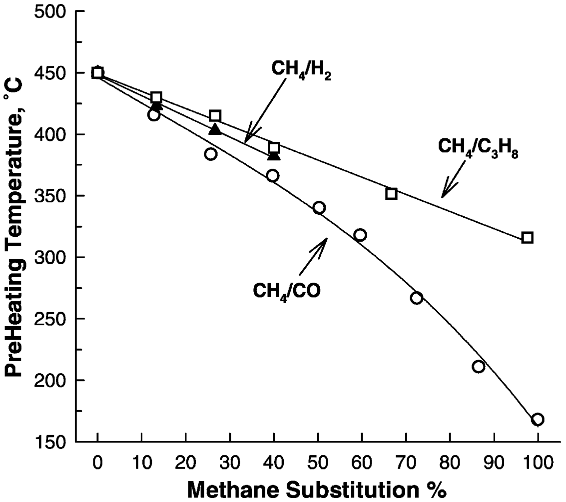

Fig. 4. Minimum pre-heating temperature for ignition over supported $LaMnO_3$ catalytic monolith for different binary fuel mixtures at fixed heating value (1 kJ/l, equivalent to 3% CH_4). GHSV = 16 000 h^{-1}.

Light-off for pure CO (8.54% v/v) and C_3H_8 (1.18% v/v) in air is controlled by the kinetics of heterogeneous oxidation of these fuels and is achieved, respectively, at 160 and 310 °C. For safety reasons hydrogen rich mixtures were not tested because inside flammability limits already at room temperature. Minimum pre-heating temperatures for the light-off of CH_4/C_3H_8 mixtures follow a linear trend over the entire range of compositions; on the other hand, a distinct curvature appears in the case of CH_4/CO mixtures, reflecting a progressively better use of the heating value of the CO fraction. Indeed, at the lower temperatures required to ignite CO rich mixtures, heat losses by radiation from the monolith are strongly reduced and thus the internal heating of the catalyst is closer to the adiabatic value.

Fig. 5 shows a representative comparison of the catalyst behaviour during light-off of the three binary fuel mixtures at a fixed methane substitution level (25%) with respect to the case of a pure methane feed. Temperature profiles of the catalyst (Fig. 5a–c: respectively, T_1, T_2, T_3) and conversions of the various fuels (Fig. 4d and e) are reported as functions of the pre-heating temperature, varied during this set

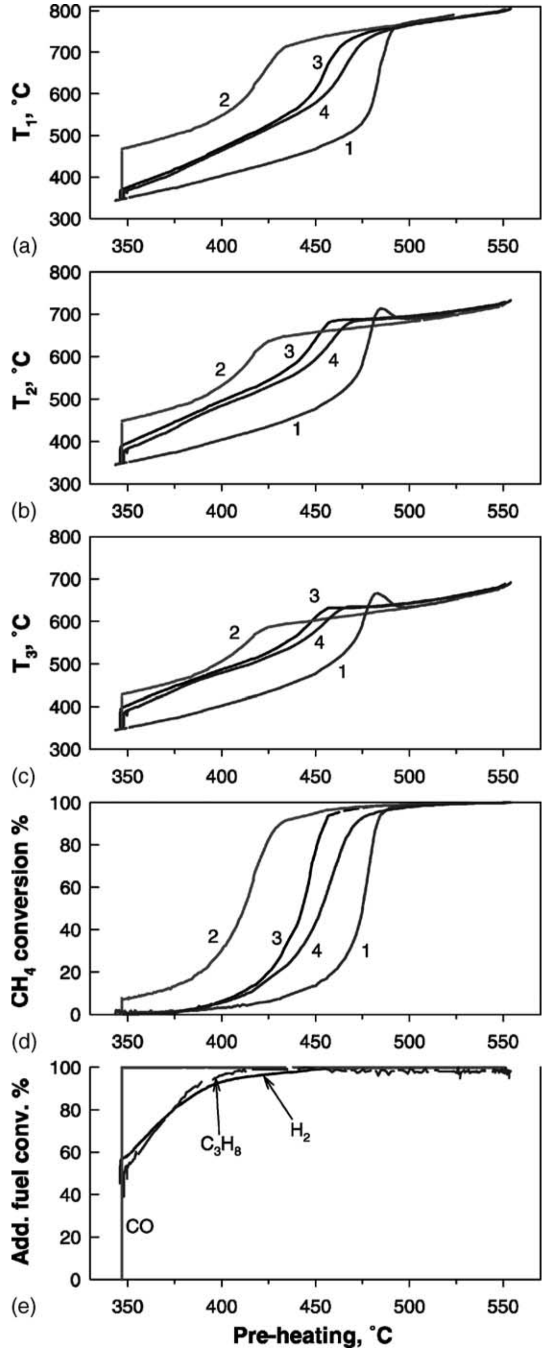

Fig. 5. Temperature profiles inside the catalyst (a–c), methane conversion (d) and additional fuel conversion (e) as a function of the pre-heating during light-off experiments for the following energetically equivalent fuel mixtures: (1) pure CH_4 3%; (2) CH_4 2.2%+CO 2.2%; (3) CH_4 2.2%+H_2 2.6%; (4) CH_4 2.2%+C_3H_8 0.31%; same temperature ramp (≤3 °C/min) from 350 to 550 °C.

of experiments from 350 to 550 °C (at the same rate, ≤3 °C/min).

- Pure methane: at the lowest temperature methane results almost unconverted over the catalyst, whose temperature profile is flat and follows the imposed heating ramp. Above 450 °C heterogeneous oxidation becomes fast enough to ignite the mixture, producing a steep increase in methane conversion. In agreement with previous results [10 and references cited therein], ignition occurs at the exit end of the monolith where the temperature is initially higher due to the heat of reaction transferred forward by the gas flow. Thereafter, the reaction front propagates backwards accompanied by a typical temperature wave, which, travelling all the way back to the proximity of the inlet section, results in the temperature peaks registered both at the outer (T_3) and intermediate position (T_2).
- CH_4+CO: the CO fraction of the fuel is completely oxidised as soon as fed to the catalytic monolith pre-heated at 350 °C, causing the sharp increase of temperature shown in Fig. 5a–c. Since the catalytic activity for CO oxidation is high at this temperature level, the (CO) reaction front appears immediately localised close to the entrance of the reactor (the hottest zone of the monolith). The additional, internal pre-heating of the catalyst, obtained through the combustion of CO, causes a clear shift towards lower temperatures of the methane conversion plot, which also displays a more shallow profile, probably due to the lower CH_4 concentration. Contrarily to the case of pure methane, temperatures at all different axial positions inside the catalyst raise monotonically, and the highest values are always measured at the entrance (T_1). This implies that the reaction front of CH_4 combustion does not travel along the reactor and is positioned close to the inlet section as soon as light-off occurs, producing an heat wave which this time moves in the same direction of the flow.
- CH_4+H_2 and CH_4+C_3H_8: these mixtures are characterised by an intermediate behaviour between the two previous cases. Indeed, at 350 °C both hydrogen and propane are converted only by about 50%. In these cases, it is not possible to locate a well defined reaction front for these species, since it is spread over the whole length of the monolith, which

shows an increasing temperature pattern along the axial direction but is globally colder than with CO. It is worth noting that, although conversion plots of H_2 and C_3H_8 are almost completely overlapped (Fig. 5e), the light-off curve of methane fraction is steeper and shifted to lower pre-heating temperatures in the presence of hydrogen (Fig. 5d). The catalyst appears slightly hotter with the addition of H_2 rather than C_3H_8, even if both fuels are at the same conversion level, and in fact this happens already when methane is not converted yet. These circumstances are probably related to the peculiar diffusion characteristics of hydrogen (Lewis number >1) which can cause a larger temperature increase of the catalytic surface under mass transfer controlled regimes [21]. The effect tends to disappear at higher pre-heating levels: since reactions are completed within the first millimetres of the monolithic catalyst, i.e. before the first measuring position T_1, temperature profiles for the different mixtures overlap. In fact, the remaining part of the reactor works as an heat exchanger for the gas [10,12], characterised by the same features independently from the fuel mixture employed.

Although maximum catalyst temperature are deliberately kept below 850 °C to preserve initial catalyst activity, very high conversion levels for all the different fuels can be achieved, as shown in Table 2 for the representative experiments of Fig. 5 at steady pre-heating of 550 °C. In particular, the combustion of pure methane proceeds only through heterogeneous deep oxidation reactions without production of CO (<2 ppm). Small amounts of unreacted CO and H_2 (roughly 10–20 ppm) are found in the product stream when these fuels are co-fed to the system, while NO is always below the detection limit of 2 ppm, as expected in this temperature range.

Table 2
Emissions of unconverted fuel (on a dry basis) at final steady state conditions for experiments of Fig. 5 (pre-heating 550 °C)

Fuel mixture	Emissions (ppm)		
	CH_4	CO	H_2
CH_4 (3%)	65	2	–
CH_4 + CO (2.2 + 2.2%)	70	20	–
CH_4 + H_2 (2.2 + 2.6%)	20	0	10
CH_4 + C_3H_8 (2.2 + 0.31%)	15	0	–

Preliminary simulations of homogenous reactions performed with a detailed combustion mechanism (GRI_Mech 3.0 [23] implemented on CHEMKIN-PLUG software for the description of an isothermal plug flow reactor, run for the same contact time of catalytic experiments) point out that almost no conversion has to be expected for CO, CH_4 and their mixtures below 850 °C; on the other hand, a significant contribution from gas phase combustion of hydrogen and propane is likely to appear above 670 and 820 °C, respectively (Fig. 6a and b).

One important aspect emerging from Table 2 is the remarkable reduction of unconverted methane, from roughly 65–70 ppm measured both in the case of pure CH_4 and CH_4 + CO, to 15–20 ppm for the CH_4 + H_2 and CH_4 + C_3H_8 mixtures. This might be explained by marked promoting effect on the gas phase oxidation of CH_4 exerted by hydrogen and to a lower extent by

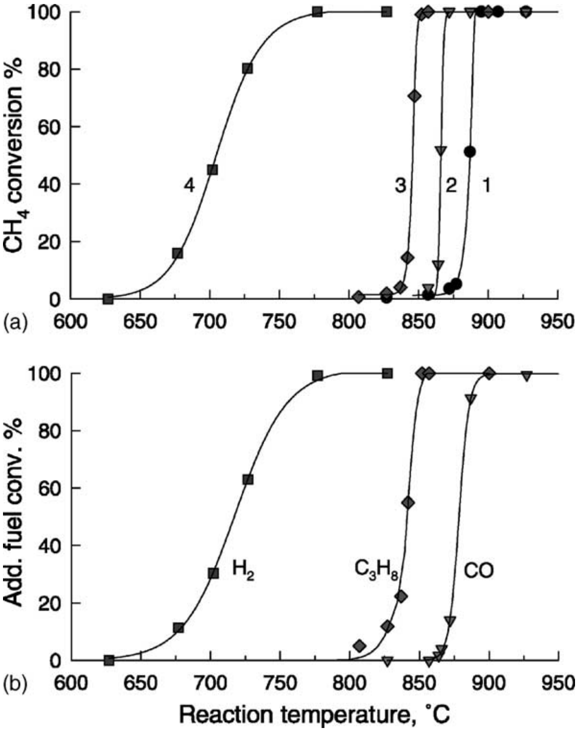

Fig. 6. Predicted conversions from detailed purely homogeneous reaction scheme GRI_Mech ($\tau = 0.185$ s at room temperature). (a) Conversion of the methane fraction for the case of: (1) pure CH_4 3%; (2) CH_4 2.2% + CO 2.2%; (3) CH_4 2.2% + C_3H_8 0.31%; (4) CH_4 2.2% + H_2 2.6%. (b) Conversion of the corresponding added fuel.

propane, that causes a progressive shift of the methane conversion plots in Fig. 6a. Indeed, the formation of a larger pool of highly reactive radicals reduces the temperature for homogeneous light-off of CH_4 combustion to levels very close to those of pure hydrogen and propane, respectively.

3.3. Multiplicity of steady states

Steady state multiplicity typical of highly exothermic reactions was reported by several authors either experimentally [12,24] and theoretically [22] with CO, propane and methane. As reported in Fig. 7, experimental runs performed starting from an ignited condition and subsequently decreasing by steps the pre-heating temperature show that the catalytic combustor exhibits different values for the ignition and extinction temperatures, producing an hysteresis (shaded region in Fig. 7) of about 100 °C in the case of pure methane in air. Moreover, two stable steady states also exist in the whole range of the $CH_4 + CO$ mixtures with constant heating value, even if the hysteresis tends to shrink at intermediate compositions ($\Delta T = 52\,^{\circ}C$ for 50% substitution). In fact, extinction is clearly identified when feeding only methane: the reaction front progressively moves towards the exit section of the catalytic reactor, and, at about 345–350 °C, the conversion drops from 96 to 1% displaying an on–off behaviour. The picture markedly changes decreasing the CH_4 fraction in the binary fuel mixture: blow-out becomes more smooth and difficult to assign with precision, because CO is still completely converted while catalyst temperatures are already too low to burn all of the methane. For this reason, in analogy with T_{ig}, the extinction curve of Fig. 7 represents the locus of external pre-heating temperatures below which the overall energy conversion falls to less than 90%.

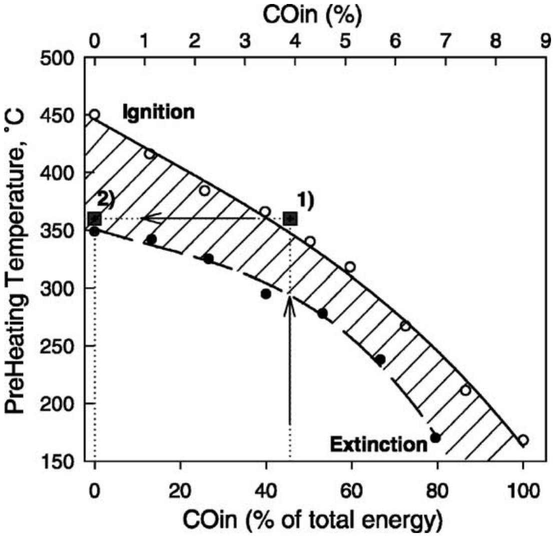

Fig. 7. Hysteresis between steady state light-off (○) and blow-out temperatures (●) for $CH_4 + CO$ mixtures at fixed heating value (1 kJ/l, equivalent to 3% CH_4) over the $LaMnO_3$-based monolith catalyst (flow rate: 60 N l/h).

It should be also noticed that pre-heating temperatures for blow-out, in contrast to light-off, vary significantly with the total flow rate in such experimental rig (far from adiabatic), according to the higher maximum temperatures reached under ignited conditions when the power generated is larger [12]. As already observed, partial substitution of methane with a more reactive fuel allows to light-off the system at lower pre-heating temperatures; once ignition has been attained, the existence of a well defined and large hysteresis loop makes it possible to switch back to only methane in the feed, keeping the system working properly at the same pre-heating without blow-out. This concept is illustrated in Fig. 7: in correspondence of the point denoted (1), ignition can be obtained with 4% of CO in the fuel–air mix at 360 °C, a value close to the compressor discharge temperature of a gas turbine and easily attained in regenerative burners. Moreover, this pre-heating level is sufficient to sustain stable ignited operation of the catalytic burner also switching to an energetically equivalent feed of pure methane (point 2). Fig. 8a shows the transient response of the catalytic reactor to the sudden change in the nature of the fuel, which at time zero is switched to pure methane, after having achieved steady state conditions with the $CH_4 + CO$ mix.

It clearly appears that the overall fuel conversion (in terms of energy) remains basically unchanged (dash line in Fig. 8a), regardless of the lower reactivity of methane. In fact the catalyst cools down in the first section (T_1), while all of the other zones become progressively hotter. The reaction front first moves forward along the monolith accompanied by the typical heat wave, but then stops and slightly inverts its direction (as confirmed by the minimum in the profiles of T_1 after 25 min and the corresponding maxima for

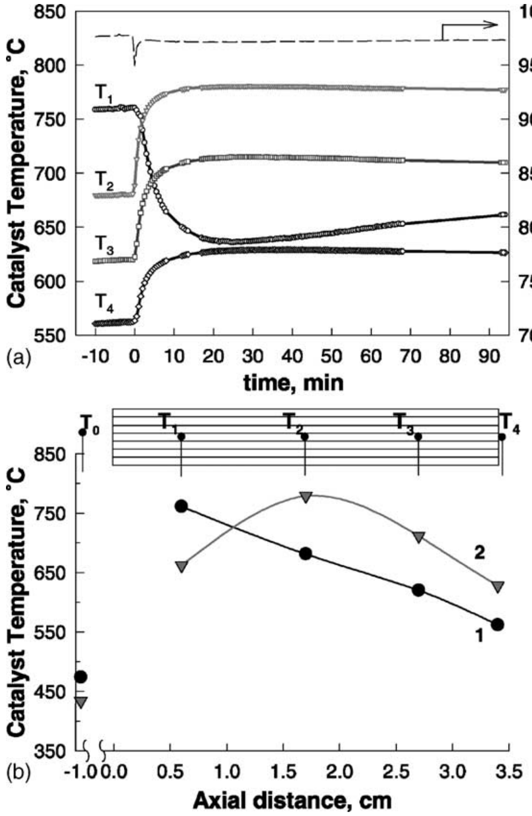

Fig. 8. (a) Transient response of catalytic burner to the change in fuel mixture from (1) $CH_4 + CO$ (1.6 + 4% inlet conc.) to (2) pure CH_4 (3%) at fixed pre-heating temperature of 360 °C. (b) Comparison of axial temperature profiles in the central channel of the monolith at the two steady states.

T_2 and T_3) to finally stabilise in the middle part of the reactor.

A direct comparison of the two axial temperature patterns at steady state is reported in Fig. 8b. As previously noted, steady operation above the minimum ignition temperature of any specific mixture is characterised by a reaction front positioned very close to the entrance (curve 1); the following part of the monolith cools down because of the absence of heat generation and contemporary losses towards the surroundings. Part of the heat is transferred upwind of the catalysts through radiation from its hot inlet surface: this causes the temperature increase recorded by the thermocouple at T_0 located inside the blank monolith preceding the catalytic module. The switch to a less reactive fuel and the consequent repositioning of the reaction front ahead along the monolith reduces this effect and spreads the oxidation of methane over a larger portion of the catalyst, even if the peak temperature appears almost unchanged (curve 2 in Fig. 8b). On the other hand, a larger radiation heat flow is obtained from the end section of the monolith.

3.4. Light-off with CO addition

The possibility to use the catalytic oxidation of an auxiliary, highly reactive fuel instead of an external preburner is examined in Fig. 9, which shows that given a mixture of 3% methane in air it is possible to ignite it at progressively lower pre-heating temperatures by adding correspondingly higher quantities of CO to the feed. The amount of CO required for ignition of the methane feed is mainly controlled by the temperature increase obtained over the catalyst through its combustion.

Actually it should be noticed that complete ignition is always obtained at catalyst temperatures slightly above 450 °C normally required with the

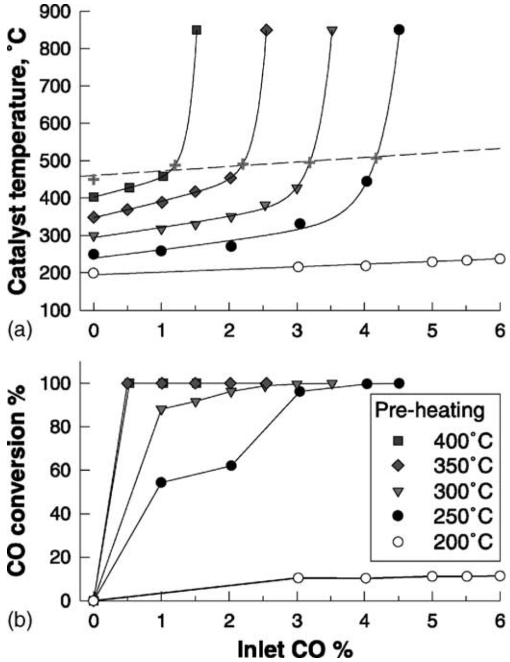

Fig. 9. Catalyst temperature T_1 (a) and CO conversion (b) as a function of the inlet CO concentration in addition to 3% methane–air mixture at different pre-heating levels.

external pre-heating and no CO addition (dashed line in Fig. 9a). This circumstance, coupled with the increasing trend of the light-off temperature when larger amounts of CO are burnt to heat the catalyst, points to a lower methane combustion rate possibly related to depletion of the gas phase O_2 and consequent CO_2 formation: these factors are, respectively, expected to slow down and partially inhibit the kinetics of methane oxidation over the perovskite-based catalyst [9].

As long as the inlet temperature of the mix is above 350 °C carbon monoxide is completely oxidised at any concentration level (see Fig. 9b) and therefore it can be safely used as an igniter without problems of emissions before complete light-off. On the other hand, at lower pre-heating temperatures, there is a progressively larger minimum concentration of CO which is required to sustain its own complete conversion over the relatively cold catalyst.

4. Conclusions

The following conclusions can be drawn from the present study on the catalytic combustion of gaseous fuels over monoliths wash-coated with γ-Al_2O_3 impregnated with $LaMnO_3$:

- Individual fuels display the reactivity order $CO > H_2 \geq C_3H_8 > CH_4$. The catalytic activity is increased by a factor that varies from 1.8 to 53 with respect to substituted hexaaluminates depending on the kind of fuel; the difference in reactivity between CO and CH_4 is reduced by order of magnitude.
- Pre-heating temperatures for light-off of catalytic combustion of methane can be lowered by a partial substitution with any of the more reactive fuels; the extent of this reduction follows the reactivity order reported and essentially corresponds to the increment of catalyst temperature due to the heat release from the heterogeneous oxidation of the auxiliary fuel.
- The high activity towards methane combustion enables to obtain complete conversion of binary fuel mixtures also in correspondence of low catalyst temperatures ($\leq$800 °C) mainly through heterogeneous reactions especially for CO and CH_4. Moreover, the presence of H_2 or C_3H_8 appears to enhance the role of CH_4 gas phase oxidation.

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