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Review

New concepts for power production by catalytic combustion: A short review

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ABSTRACT

This paper shortly reviews the main features of new concepts for power production by Catalytic Combustion (CC). In particular, the main issue of fuel-rich combustion, that has been recently proposed as a preliminary conversion stage for gas turbine (GT) burners, is herein critically examined in terms of active phases, physical and geometrical features of substrates and sulphur resistance. Moreover, in the last few decades, a huge interest towards Integrated Gasification Combined Cycle (IGCC) plants, in which several liquid or solid fuels are converted into “synthesis gas”, has increased the attention towards the study of the lean combustion of fuel mixtures containing H_2 and/or CO at conditions relevant for GT power systems. The main results of high pressure catalytic combustion of syngas have been reported. Another recent research subject is the application of CC in the micro-power generation, which was attractive as an alternative to batteries for small and/or portable devices. As a matter of fact, in this context, the use of catalytic combustion appears the better and only viable choice since the micro-scale combustion is characterized by an elevated surface-to-volume ratio involving problems for homogeneous combustion and thus favouring the catalytic one. The most important topics influencing the stability map of micro-combustors such as construction solutions, materials choice and a more reactive fuel addition (i.e. H_2) are briefly critically presented in this short review. Moreover, new concepts such as hybrid micro-combustors are herein presented as an interesting route to enlarge the operating window.

KEYWORDS: catalytic combustion, fuel-rich combustion, high pressure, syngas, micro-combustion

INTRODUCTION

Catalytic combustion (CC) has been recognized as a clean, safe and promising technology for the conversion of mixtures beyond their flammability limits at relatively low temperatures [1, 2]. As a consequence, CC has been firstly studied mainly for two purposes: i) for the VOC abatement as it occurs in the three way catalysts for example; ii) as an alternative route to produce power and heat with low environmental impact. As a matter of fact, the high combustion efficiency attainable also at relatively low temperatures, allows the simultaneous reduction of CO, unburned hydrocarbons and nitrogen oxide emissions. Moreover, the use of natural gas as feed is not related to SO_x emission, due to the availability of desulphuration units. Thus, great efforts have been directed to develop catalytic combustors for Gas Turbine (GT) systems. A schematic drawing of such a system is reported in Figure 1a.

A suitable catalyst should show several features due to the different needs of the combustion process. In particular, low ignition temperatures, possibly close to the compressor outlet temperature (290-450°C depending on load), are required and, as a consequence, catalyst should

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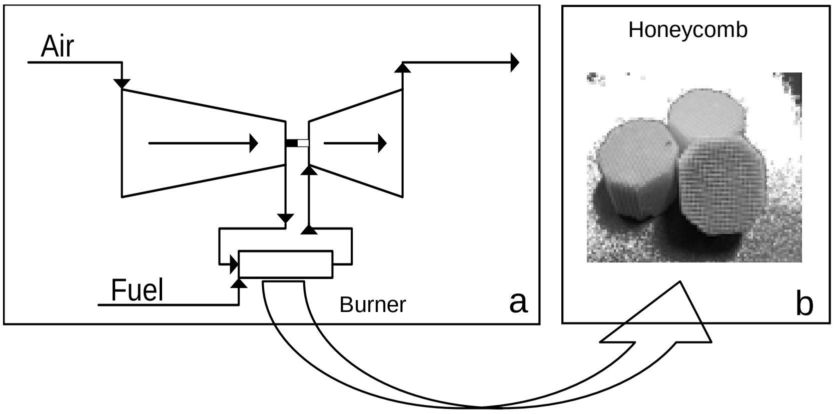

Figure 1. Schematic drawing of a gas turbine (a) and ceramic honeycombs used as catalyst substrates (b).

show high activity at low temperature. On the other hand, a catalytic combustion process is carried out at relatively high temperatures (at least 900°C-1000°C), but the turbine inlet temperature is even higher, thus catalyst should be stable at these temperatures. Moreover, mechanical resistance is required due to the stresses related to the high velocities of the gas flow through the catalyst. Starting from the last issue, the use of structured catalyst, i.e. ceramic or metallic honeycombs (Figure 1b) coated with thin layers of active phase, allows to prepare catalytic systems not only showing high mechanical properties but also very low pressure drops and high surface-to-volume ratios.

About the active phase, three main classes can be identified: i) noble metals, ii) metal oxides, iii) hexaaluminates [2, 3]. Noble metal catalysts show very high activity and relatively low light off temperatures; they are generally used for VOC abatement at low and medium temperature as it occurs in three way catalysts. The major drawback is related to their rarity, and as a consequence cost, and tendency to volatilize and/or sinter at high temperature, which limit their use to Pd and Pt only. While Pt is the most active towards H_2, CO and light C_{2+} hydrocarbons, Pd is the best active phase for methane total oxidation and, as a consequence, it was extensively studied for NG-fuelled GT. At low temperature, the catalyst is in an oxidized form PdO_x that is the most active, but increasing the temperature, about 800°C, the reduction to metallic form occurs with a consequent loss of activity. Groppi *et al.* [4] have shown the possible occurrence of two different types of palladium oxide with different activity for methane oxidation. The first PdO species is supposed to be transformed into the second one increasing the temperature; however, the change occurs at lower temperatures than for the PdO/Pd transformation. This process is reversible, re-oxidation occurring at about 600°C in air [5, 6]. Since the re-oxidation reaction is very slow and occurs at a temperature lower than that of the reduction, hysteresis phenomena happens leading to instabilities in performance of catalytic combustion [7]. It is known that the decomposition temperature of PdO is a function of the operating pressure [8].

Several authors proposed to exploit the self-regulating capacity of the catalyst to preserve itself from sintering due to high temperature [5, 9]. As stated noble metals undergo sintering and volatility phenomena above 800°C. For example, it was estimated that an exposure of 15 h at 1000°C is enough to cause the loss of 70% of the original Pt loading [9].

The supports over which noble metals are dispersed can play a relevant role, in not only improving sintering resistance but also improving the catalytic performance. This is the case of CeO_2 which, thanks to its oxygen fast release from its lattice, was proven to assist Pd in surface O_2 bonding, thus slowing the transition to Pd metallic and minimising its reduction in activity [6]. Therefore Pd/CeO_2-ZrO_2 systems have also been studied [10].

Amongst different types of metal oxides (single, doped metal oxides, perovskites, spinels and other mixed metals) perovskites have been extensively considered as total oxidation catalysts [3]. They are a group of mixed oxides represented by the general formula ABO_3 with a cubic structure that is similar to $CaTiO_3$, in which the larger cation A has a dodecahedral co-ordination and the smaller B cation has a six-fold co-ordination. Moreover, the robustness of the structure permits the partial substitution of A and B cations with metals with a different oxidation state ($A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$). The partial substitution results in the profound modification of the activity since it leads to the formation of structural defects which influences catalytic activity of the material [11]. Some of these oxides show significant activity, similar to that of platinum under specific conditions, already at relatively low temperature [11-13]. To date, the best active phase formulations for methane are those in which A site are occupied by La or La-Sr and B site are occupied by Co, Fe, or Mn [13]. For instance, $LaMnO_3$ is considered the most active formulation [14]. Nevertheless, the application of perovskites is limited by their low surface area. Moreover, operation at temperatures above 800°C leads to sintering of perovskite-oxides caused by the 3D growth of crystals. After exposure to temperature above 900°C, the surface area diminishes and consequently catalytic activity decreases [15]. In order to overcome these problems, different research groups have dispersed active phases on high surface area supports like La-stabilized alumina or La-stabilized MgO or spinels with an increase in activity and thermal stability [16]. One of the most employed supports is γ-Al_2O_3, characterized by a specific area of about 200 m^2/g. Nevertheless, close to 1000°C, γ-alumina undergoes a phase transition to α-alumina, which exhibits a lower specific area. In order to overcome such an inconvenience, it has been proposed to kinetically inhibit γ to α phase transition, by adding small quantities (typically 5wt % as regards the total amount of support is considered enough) of lanthanum oxide to the γ-alumina lattice [15].

In order to increase perovskites activity towards combustion reactions, the use of bi-functional catalysts has been proposed, in which perovskite phase is promoted by small amounts of noble metal [17-20]. Perovskite, besides exhibiting its own catalytic activity, may be an ideal environment to host noble metals causing a high dispersion of the active phase and limiting noble metal volatilization and sintering. Moreover, particular synergies may occur especially due to eventual interactions of the noble metal with the extra lattice oxygen of perovskites. On the other hand, the noble metal, even if in small quantities but well-dispersed, may increase catalyst activity at low temperature. Despite numerous studies concerning catalytic combustion on Pd-perovskite catalysts [17, 19-20], Pt-perovskites are less studied. Recent works of Giebeler and co-workers [18] and Scarpa *et al.* [21] demonstrated that platinum promoting is not effective in enhancing perovskites activity towards methane combustion at least on oxidized samples.

The highest thermal stability is showed by the last class of catalysts, the hexaaluminates, very suitable for very high temperature applications. So they have been extensively studied since the pioneering work by Arai and co-workers [22, 23]. The general formula of these materials is $AAl_{12}O_{19}$ where A is an alkaline or alkaline-earth element (La or Ba). The high thermal stability is derived by its lamellar structure, which consists of stacked spinel blocks separated by a monolayer of oxides. The presence of the Ba or La cation blocks the crystal growth thus conferring superior stability properties (surface area >20 m^2/g at T >1200°C and stable operation till 1600°C).

Nevertheless they exhibit very low activity. In order to improve the activity, great efforts have been made to dope these materials. It should be however noted that, differently to perovskites, the crystal structure is less available for partial substitution of La or Ba cation with Sr or Ca. Also transition metals like Fe, Co and especially Mn could be introduced in the lattice structure thus improving activity towards methane combustion but only slightly. In fact, the activity of these materials towards methane combustion remains very low compared to Pd. It is worth noting that, with respect to other groups of catalysts, the difference among the activities towards the total oxidation of alternative fuels (carbon monoxide, hydrogen, syngas and diesel) is less significant [24]. Extruded monolith of substituted hexa-aluminates were initially proposed and employed as high temperature catalytic stages in GT application [25].

As it clearly appears from the above considerations, notwithstanding several efforts, a single catalytic system is unable to fulfil all process requirements. As a consequence, complex process designs including firstly several catalytic stages (with different active phases progressively with decreasing activity and increasing thermal stability) [25] and afterwards including an additional homogeneous stage [26, 27] have been proposed.

This "hybrid" combustion concept consists in a low-medium temperature catalytic combustion zone followed by a high temperature gas phase combustion zone. To date, "hybrid" solutions are preferable due to the higher temperatures achievable at the turbine inlet (≤1400°C) [28] and the much higher throughputs attainable (i.e. compactness of the combustor) with respect to the former solution [29].

Two main strategies have been proposed for hybrid (catalytic/homogeneous) systems which will be described in the following.

Even if recent technologies based on hybrid concepts are commercialized (Xonon Combustion System by Catalytica [30], RCL Catalytic Combustor by Precision Combustion [31]), a wide diffusion of catalytic combustion in power and heat production was not achieved especially for large, Heavy-duty GT [27].

On the other hand, in a future scenario with more stringent regulations regarding NO_x emissions, catalytic combustion could be the most effective choice especially for small size (≤5MW) GT [32].

Catalytic combustion has recently received a renewed interest due to new ideas. In particular, in this paper new concepts for power production by catalytic combustion have been briefly revised, such as fuel-rich combustion of light hydrocarbons, high pressure combustion of syngas (or hydrogen enriched mixtures) and micro-combustion.

Fuel-rich catalytic combustion

According to the above considerations, catalytic combustion has been generally proposed as a stage of a complex combustion system, the so-called Catalytically Stabilized Thermal (CST) combustion [33, 34]. In the most common case, the fuel-air mixture, with a composition in the fuel-lean region, is fed to the catalyst, generally Pd-based, and partially converted to combustion product. The hot gases are completely burnt by a homogeneous flame downstream and stabilized by the catalyst. A drawing of the CST combustion is reported in Figure 2.

Recently an alternative to this approach has been proposed based on a catalytic module working under fuel-rich conditions (Figure 3). The fuel is added to a fraction of the air, resulting in a fuel-rich mixture, which is catalytically converted to both partial and total oxidation products that are subsequently mixed with excess air to complete the combustion in an ultra-lean homogeneous flame [35]. In another approach, only a small fraction of fuel is catalytically converted under fuel-rich condition and the remaining is injected into the by-pass air stream. In this way the catalytic module acts as a pilot imparting stability to the ultra-lean main flame and replaces the diffusion or partially premixed pilot flame in DLN systems [36]. Several advantages

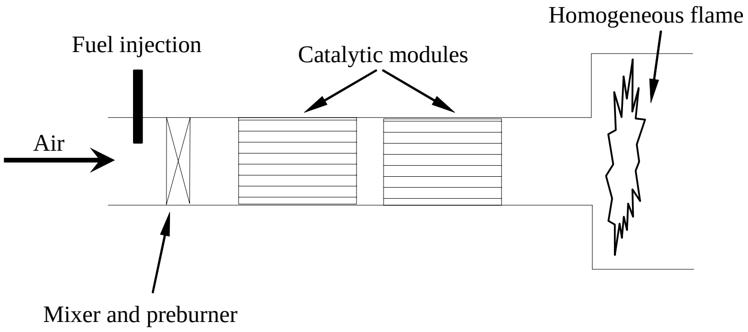

Figure 2. Catalytically Stabilized Thermal (CST) combustion.

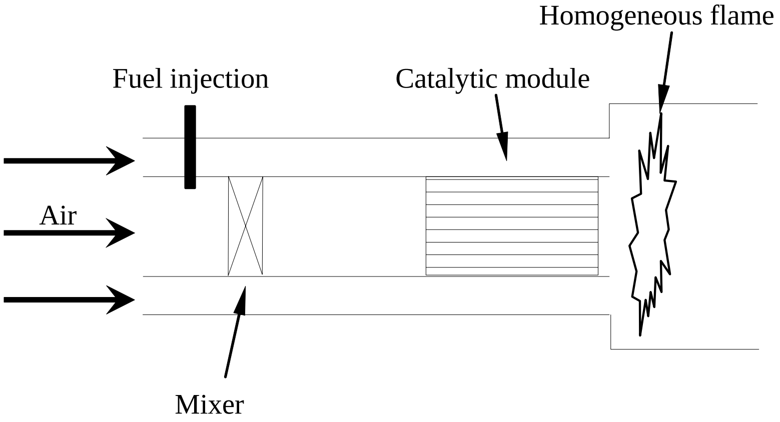

Figure 3. Rich Catalytic Lean combustion.

can be obtained by fuel-rich methodology. First of all, the presence of syngas in the hot product stream from the catalytic zone can help in stabilizing lower temperature flames in the burnout zone, thus reducing NO_x emissions [35]. Moreover, fuel-rich mixtures show a lower light off temperature [37], thus eliminating the pre-burner shown in Figure 2 and not present in Figure 3, where significant NO_x amounts are produced. Further advantages are related to an intrinsically safer operation of the fuel-rich catalytic stage which is not prone to flashback issues, and to the non-sooting characteristic of the diluted syngas secondary flame, regardless of the specific fuel fed to the first catalytic stage. From the point of view of the catalytic system, the moderate extent of the catalytic reaction, due to the limited oxygen availability, the catalyst is prevented from reaching very high temperatures even in the presence of a not perfectly mixed feed, thus preventing deactivation and significantly improving its durability [35]. Moreover, the absence of adsorbed surface oxygen minimizes catalyst volatilization as noble metal oxide [35].

As it clearly appears, the catalyst performs the partial oxidation of the fuel and, as a consequence, its features are the typical ones of catalytic partial oxidation catalysts. From a general point of view, considering also the literature of the catalytic partial oxidation (CPO) reaction and starting from the first works [38-41], two main classes of catalysts have been studied, containing Ni [42-50] or noble metals [45, 51-63] as active phase. In order to minimise pressure drops at the high flow rates, the realisation of high void fraction reactors is necessary, as reported above. Several configurations have been proposed like honeycombs [55, 57, 64, 65], foams [51, 62], spheres [51] and wires [55, 58]. Although more expensive than Ni-based catalysts, noble metals (generally Pt and Rh) appear to be very attractive because of their high activity, allowing the development of processes at short contact time (SCT), and no coke formation [39]. However, this class of catalysts suffers from deactivation due to the formation of hot spots [39], caused by the rapid CH_4 oxidation leading to a mixture of partial and total oxidation products, as proposed by Lyubovsky *et al.* [58], Horn *et al.* [62] and Liu *et al.* [64]. For obtaining effective catalysts with an optimised use of the noble metal, precious metals have been supported onto different materials (eventually modified with oxygen carriers), in order to obtain good dispersion of the active phase and to reduce deactivation by volatilisation and sintering. In particular, it has been demonstrated that the addition of oxygen carriers like MgO [54, 60] and CeO_2 [52, 61, 63] leads to higher performance for both Pt and Rh. Also the addition of small Rh amount to a perovskite has been demonstrated to be effective in enhancing catalytic properties [66, 67]. In particular, the authors showed that $LaMnO_3$ perovskite is able to improve not only steady state performance with respect to a catalyst containing only rhodium, but also to reduce light off temperature (Figure 4). Moreover, the same authors showed that the reduction of the Rh content is coupled with reduced CH_4 conversion [67], related to a decreased activity

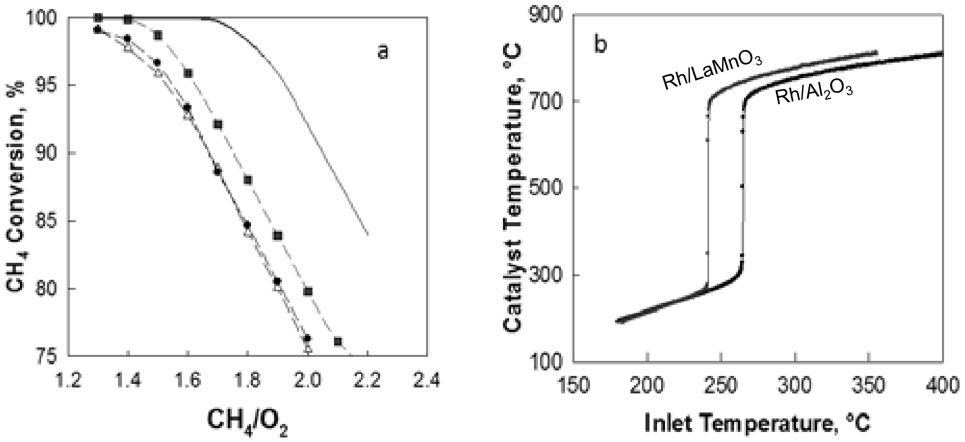

Figure 4. a) CH_4 conversion, under pseudo-adiabatic conditions as a function of CH_4/O_2 feed ratio over Rh/Al_2O_3 (●), $Rh/LaMnO_3$ (■) and $Rh/LaCoO_3$ (Δ) monoliths. Solid lines correspond to equilibrium among gaseous species only. b) Light off temperature of fuel-rich catalytic combustion over $Rh/LaMnO_3$ and Rh/Al_2O_3 monoliths under pseudo-adiabatic conditions. CH_4/O_2 ratio = 1.8 (Adapted from [66]).

towards steam reforming reaction occurring in the second part of the catalyst, i.e. after complete oxygen conversion.

Moreover catalytic performance strongly depends on the substrate features (i.e. geometry, thermal conductivity) [39, 51, 66-70]. As a matter of fact, Schmidt and co-workers showed that the deposition of Rh onto α-alumina spheres resulted in superior catalytic performance with respect to a catalyst containing the same amount of noble metal deposited onto a foam monolith [51]. The Authors suggested that the difference should be related to different heat transports, leading to blowout occurrence in the case of foam monolith. Different conclusions have been addressed by Maestri *et al.* [71] simulating different structured and packed bed reactors, honeycombs and foams showing better performance than packed beds. But also in this case the differences among the substrates have been attributed to changes in transport phenomena (and in particular heat transfer). Moreover, they found that, while oxygen conversion is under mass transfer limitations, methane conversion depends on a more complex mechanism, involving both surface kinetics and mass transfer, their relative ratio depending on flow rate, due to higher surface temperatures. Landi *et al.* [67] studied the effect of honeycomb cell density on catalytic performance of $Rh/LaMnO_3$ catalysts; catalytic performance appeared sensitive to channel dimensions (Figure 5), cell density increasing from

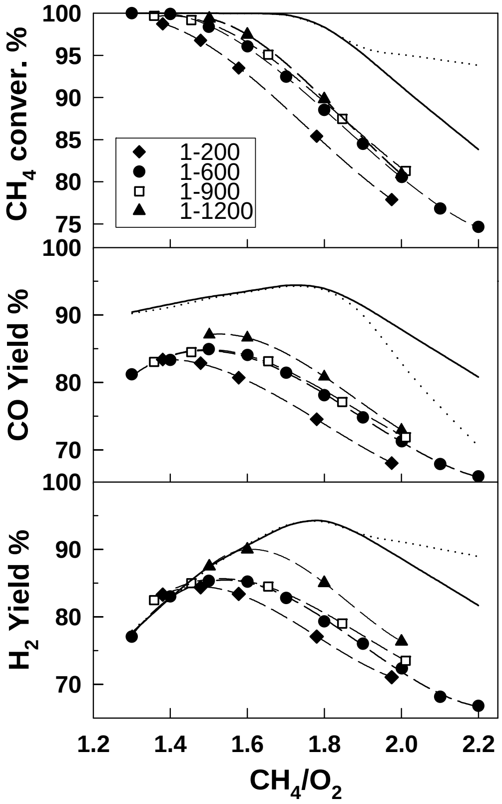

Figure 5. CH_4 conversion, CO and H_2 yields as a function of CH_4/O_2 feed ratio over $Rh/LaMnO_3$ cordierite honeycombs with different cell density. Solid lines correspond to equilibrium among gaseous species only, whereas dotted lines also include solid carbon formation (Adapted from [67]).

200 to 1200 cpsi. This was due to a combination of factors including higher catalyst loadings (related to higher exposed surface areas), thus promoting steam reforming occurrence which is kinetically controlled, and higher gas-surface heat transfer, improving the thermal management of the reactor.

The thermal management is a key point for a partial oxidation catalyst; as a matter of fact, high temperatures can be attained in the first part of the reactor, i.e. where oxidation reaction occurs, causing deactivation phenomena related to sintering and/or volatilization of the active phase or to the overcoming of the maximum attainable temperature of the substrates, while the temperatures can drastically decrease in the second part of the reactor, where steam reforming occurs, down to levels causing kinetic limitations and consequently an incomplete fuel conversion. The use of highly conductive substrates, such as SiC as reported in [69], leads to improvement in the performance of the catalytic system; this is due to the ability of the SiC to fast drive the heat produced in the oxidation zone to the reforming zone, as suggested by comparing the temperature profiles measured inside a cordierite and SiC honeycomb monolith (Figure 6), thus promoting reforming activity. The beneficial effects of highly conductive substrates are not limited to the enhanced performance, but the reduction of the temperature peak in the first part of the reactor can be related to longer durability of the catalyst due to the reduction of sintering phenomena occurring at elevated temperatures.

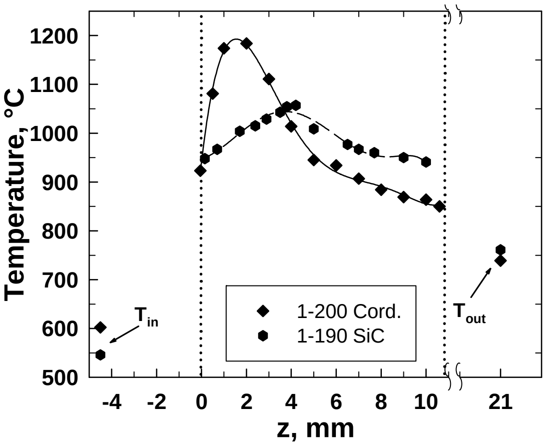

Figure 6. Temperature profiles along the axial coordinate of SiC and cordierite Rh/$LaMnO_3$ honeycomb catalysts during self-sustained partial oxidation reaction at CH_4/O_2 feed ratio = 1.7, using O_2 as oxidant. (Adapted from [67]).

Another interesting aspect recently investigated is related to the effect of sulphur compounds on the catalytic performance of Rh-based catalyst and on the development of sulphur tolerant systems. As a matter of fact, the presence of sulphur containing compounds naturally occurring in natural gas or added as odorants necessary for safety reasons can result in a sulphur concentration totalling approximately 10 ppm. The deactivation effect related to sulphur compounds is generally due to chemisorption onto and reaction with the active catalytic sites, thus inhibiting reactant access [72]. In addition sulphation of the support component can also occur, thus affecting metal-support interaction. As an example, sulphation of the support has been identified as the main cause of deactivation for steam reforming [73] and methane partial oxidation [74, 75] over supported rhodium catalysts, by reducing (i) the formation of hydroxyl species adjacent to the metal-support interface and (ii) migration of more remote hydroxyl species to the interface where they can interact with adsorbed hydrocarbon [76]. Accordingly, under moderate temperatures a more sulphating support can act as a “sulphur pump”, i.e. adsorbs and shifts sulphur compounds far from the active centres, as suggested in [77]. On the other hand, at higher temperatures the effect of the support seems less important [78], while the use of bi-metallic Pt-Rh catalysts has been revealed effective in the enhancement of sulphur tolerance under partial oxidation conditions (temperature >800°C and short contact time) [79], as well as improves the activity of Rh-based catalyst during the steam reforming of sulphur-containing fuels [80].

In conclusion, fuel-rich catalytic modules are nowadays mainly based on Rh catalysts. Significant but not sufficient efforts have been made in order to reduce the noble metal content, without a large depletion of the catalytic activity. The dispersion of small amounts of noble metal into an active matrix, such as metal oxides, acting as oxygen carriers and/or secondary catalysts, seems a way in order to make fuel-rich catalysts cheaper and effective. On the other hand, catalyst formulation, including both the active phase and the support, could be modulated in order to produce more sulphur tolerant systems. Finally, catalytic performance depends not only on active phase but also on geometrical and physical features of the substrate, especially under self-sustained reaction conditions, i.e. in the presence of large temperature and concentration profiles and significant mass and heat transfer limitations. As a consequence, after active phase selection under diluted reaction conditions, catalysts should be tested under more severe conditions and the catalytic system should be engineered by a proper choice of the substrate in terms of type (foam, honeycomb, pellet), void fraction (channel or pore dimension, particle diameter), and thermal conductivity.

High pressure combustion of syngas (or H_2 enriched mixtures)

The availability of fuel mixtures containing hydrogen and/or carbon monoxide has increased during the last years. First of all, during the last decade the interest towards what Neathery *et al.* [81] called the “pioneer plant”, i.e. a plant where the production of electricity and high value added products from coal simultaneously occurs, has increased. In particular, the electricity production takes place through a gas turbine combustion of coal gasification products (i.e. mainly CO and H_2) in an Integrated Gasification Combined Cycle (IGCC). In Italy an IGCC plant has recently been realized by API within the refinery in Falconara Marittima [82, http://www.apioil.com/ita/igcc.asp] and by ENI within the refinery in Sannazzaro [83, http://www.eni.com/it_IT/azienda/attivita-strategie/refining-marketing/raffinazione-rf/gassificatore.shtml], whose raw materials are sulfur-rich heavy oil refining residues. Therefore in recent years the research is focusing on the study of combustion of mixtures containing hydrogen and/or carbon monoxide and/or methane at the operating conditions typical of gas turbines from both chemical [84, 85] and economic [86] points of view. In particular, it should be noted that the partial or total replacement of methane, representative of natural gas, with low calorific fuels, such as H_2 and CO, is usually accompanied by a reduction in fuel mixture dilution thus resulting in adiabatic temperature and NO_x production increase even for established technologies such as gas turbines. As a matter of fact, new materials for gas turbine blades stable at higher temperatures have been investigated [28].

The interest towards the combustion of hydrogen and/or carbon monoxide rich mixtures is related to the possibility of use as fuel not only the syngas from the gasification of coal or biomass, but also other hydrogen-rich fuels such as the by-products of steel and coal industries or blends added with hydrogen not produced from fossil fuels (e.g. through water electrolysis using wind or solar energy). In particular, with regard to renewable sources emissions of greenhouse gases would be reduced. As mentioned above, the combustion of low BTU mixtures can be associated with an increase of NO_x emissions. In this context, catalytic combustion has been proposed as an alternative route to the homogeneous combustion of low BTU mixtures.

As reported in the first part of this work, a large number of papers have been devoted to catalytic combustion at atmospheric pressure and under very diluted (i.e. isothermal) conditions. Notwithstanding, “*it is not unusual to hear of catalysts that appear to have worked well in a laboratory environment but do not so when installed in a High Pressure pilot-scale rig*” [87], suggesting that the relative ratio amongst the several phenomena simultaneously occurring during catalytic combustion (external and internal mass transfer of both reactants and products, heat transfer from and to the surface and along the catalyst, surface and homogeneous kinetics) could be changed by changing the working pressure, as reported by Carroni *et al.* [8]. Nevertheless, in the last 15 years very few studies have been devoted to high pressure with respect to atmospheric combustion (Figure 7).

According to the general considerations reported in the first paragraph, noble metal catalysts, showing the highest reaction rates, have been generally investigated at above atmospheric pressure [88-92], while only few works have been devoted to mixed oxide catalysts [93, 94].

On Pt-based catalysts Mantzaras and co-workers performed both experimental and numerical

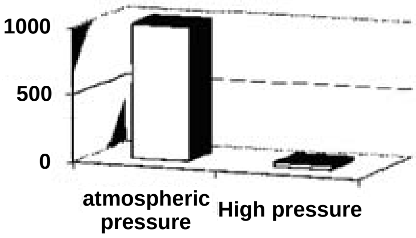

Figure 7. Number of papers devoted to atmospheric and high pressure catalytic combustion since 1995.

studies [95]. The main aim of their works was to develop a model reproducing the experimental results of syngas combustion in a wide range of operating conditions (temperature, pressure, feed composition). An in-depth discussion of the results of these works is outside the scope of this paper, but some useful results can be taken into account. First, the authors found that in order to simulate not just the overall performance at steady state but also the temperature and concentration profiles and light off behavior, it is necessary to include detailed kinetic schemes for both homogeneous and heterogeneous reactions. In particular, they found that the Deutschmann's catalytic [96] and Warnatz's homogeneous [97] reaction schemes are the best candidates to reproduce syngas combustion in a wide range of operating conditions [98]. Simulations and experimental tests have been done under steady state and transient reaction conditions; a good agreement has been found in terms of both overall performance and dynamic behavior during light off. The results about the impact of homogeneous chemistry on the catalytic reaction appear very interesting. Due to its Le number lower than 1, hydrogen generally diffuses towards the catalytic surface more rapidly than oxygen and CO, thus producing a fuel-rich mixture on the catalyst, characterized by a higher (superadiabatic) temperature, causing a more pronounced deactivation. If the gas phase combustion is taken into account, thus consuming a fraction of the fuel, hydrogen diffusion is depleted and surface temperature is consequently reduced.

It must be underlined that the schemes of Deutschmann and Warnatz are constituted by 20 and 33 reactions respectively; as a consequence they need an opportune software design and a relatively long calculation time. Thus, for engineering purposes or rough estimations of burner performance, simple reaction rate equations must be derived. As an example Boudzianowski and Miller [99] simulated a superadiabatic lean Pt-based combustor, operated up to 10 bar and fed with propane using an adapted reaction rate equation derived from Reinke *et al.* [88]. In particular, the effect of pressure has been taken into account by multiplying the reaction rate at atmospheric pressure (eq. 1) by a factor $(P/P^0)^{-0.53}$ (eq. 2).

$$R = k_0 \cdot \exp\left(-\frac{E_a}{R_g T}\right) \cdot \frac{xPM_P}{R_g T} \qquad \text{(eq. 1)}$$

$$R = k_0 \cdot \exp\left(-\frac{E_a}{R_g T}\right) \cdot \frac{xPM_P}{R_g T} \cdot \left(\frac{P}{P^0}\right)^{-0.53} \qquad \text{(eq. 2)}$$

As a consequence, the high pressure reaction rate depends on the overall pressure by a factor equal to about 0.5 (at atmospheric pressure the reaction rate is linear with respect to pressure), suggesting a sort of inhibition effect of pressure on the combustion kinetics.

Recently combustion kinetics of different fuels (CH_4, H_2, CO) on a perovskite catalyst has been investigated in the pressure range 1-10 atm [93]. Generally, the pressure effect on kinetics is positive, i.e. the apparent reaction order with the overall pressure is positive, but less than linear, as it occurs for Pt catalyst as reported above. For example, in Figure 8a the reaction rate at fixed temperature as a function of CH_4 inlet fraction and parametric in the overall pressure is reported. On this type of catalysts, a general agreement on the reaction rate expression has not been achieved. As a matter of fact, despite the large number of papers devoted to this subject, two main types of reaction rates with respect to fuel partial pressure can be identified in the literature: linear (the most common) [11 and 14, as examples] and fractional [100, 101]. As shown in Figure 8a, reaction kinetics of methane is linear only at low operating pressure, i.e. atmospheric, but by increasing this parameter the apparent reaction order with respect to fuel fraction steadily decreases down to 0.56 at 8 atm. On the other hand, the combustion rate as a function of the fuel partial pressure (Figure 8b)

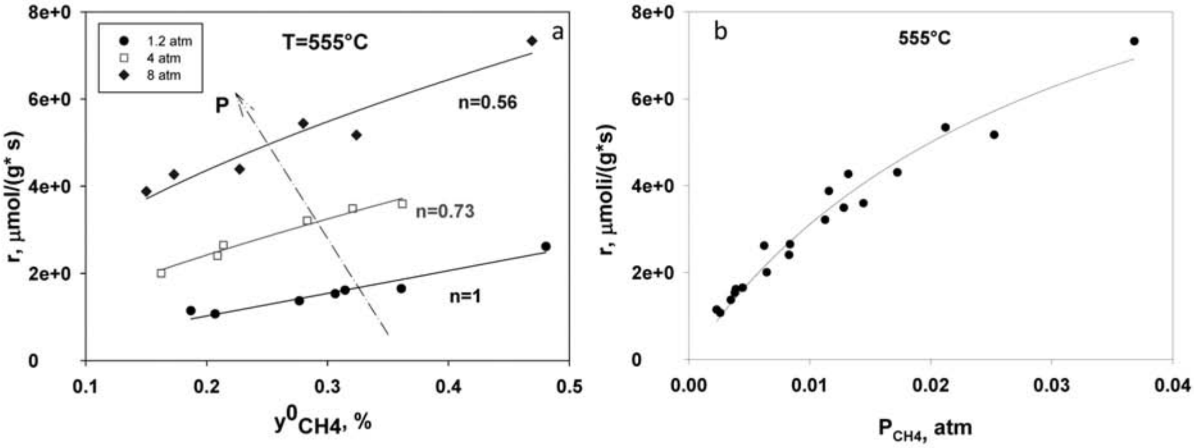

Figure 8. a) CH_4 reaction rates as a function of the inlet methane fraction and parametric in the pressure and b) CH_4 reaction rates as a function of methane partial pressure (Adapted from [93]).

can be easily regressed with a simple rate expression (eq. 3):

$$r = \frac{k \cdot P_{CH_4}}{1 + K \cdot P_{CH_4}} \qquad \text{(eq. 3)}$$

As a consequence, it appears that the two main hypotheses regarding methane combustion kinetics can be matched considering that at low fuel partial pressure, the reaction rate is well approximated by a linear regression. By increasing fuel partial pressure (by increasing the overall pressure or the fuel concentration) this approximation fails and rate expressions such as eq. 3 are necessary in order to well reproduce experimental data. This type of approach allowed to reproduce a large amount of experimental data as a function of the pressure, temperature and fuel concentration for different fuels (CH_4, H_2, CO).

On the other hand, catalytic performance can be affected by the presence of CO_2 and/or H_2O in the feed, generally unavoidable if syngas is produced by a gasification process. As an example, Andrae *et al.* [91] studied the effect of pressure on the combustion of a synthetic gasified biomass fuel with a significant CO_2 fraction in a hybrid combustor equipped with a Pt catalyst. In the model section of the paper, they reported that before ignition the major species covering the Pt surface are CO, H and CO_2.

In conclusion, catalytic combustion appears a promising route for the conversion of syngas-based fuels, eventually added with methane, in gas turbines due to the high reactivity of CO and H_2 on a catalyst. Even though a large number of papers have been devoted to catalytic combustion at atmospheric pressure, they are not easily extensible to gas turbine operating conditions, while high pressure data is very scarce in the literature, probably due to more difficult realization and management of an experimental rig operating at above atmospheric pressure. To date, papers devoted to high pressure combustion have been mainly related to noble metals catalysts, which appear a good choice for relatively low temperature applications, such as the catalytic module of a CST system. On Pt catalysts, combustion performance can be simulated by a complete model approach, taking into account mass and heat transfer, homogeneous and surface kinetics (including more than 50 reactions for H_2 and CO combustion only). More simple reaction rates have been derived for perovskite-based catalysts; from these results it can be derived that differences among the models proposed at atmospheric pressure are simply related to the limited reaction conditions applied in each case.

Micro-combustion

Micro-power generation realized by coupling a thermoelectric device and a micro-combustor, i.e. a burner with at least a sub-millimeter dimension, is a research subject of significant novelty from both a fundamental and an applicative point of view. As a matter of fact, the development of such a system, compact and light, could represent an alternative to batteries for small and/or portable devices [102]. Due to high power density of common fuels, a system showing very low overall efficiency (<5%) could replace batteries, which are characterized by very low power density. Another possible application of micro-combustion is related to the development of (micro)reformer-fuel processors [103]; in this case, combustion could provide the heat necessary to sustain endothermic reactions such as the steam reforming of the fuel.

Loss of combustion stability occurs either via extinction or blowout [104-107]. In extinction, stability is lost due to large heat losses compared to the power provided via combustion. In blowout, quenching occurs because of low residence time, resulting in incomplete fuel conversion and a considerable shift of the reaction front downstream. As a result, in microscales stable combustion occurs in a limited operating window and the challenge is to adopt a careful combustor design to enlarge it.

The wall thermal conductivity certainly plays a relevant role. Particularly, it needs to be sufficiently high to provide ignition of the cold incoming gas but it is responsible, at the same time, for the heat losses exhibited by the system. As a result, wall thermal conductivity needs to be balanced in order to provide enough preheating such as to avoid blowout but limit heat losses to prevent extinction.

Similar considerations are valid in the case of gas velocity. Particularly, a tradeoff on the total flow rate such as to generate sufficient power to prevent extinction and to avoid blowout is suggested. An approach to enhance micro-combustion stability is based on heat recovery. Heat-recovery systems include the reverse flow reactor and the heat recirculation reactor, whose effectiveness in enhancing combustion stability has been theoretically and experimentally studied [106, 108-112]. In reverse flow reactor the flow direction is periodically reversed to trap a hot zone within the reactor [109]. A heat-recirculation combustor is equipped with a counter-current heat exchanger that transfers the heat from the hot exhaust gas to the incoming reactants [106, 112]. One of the most effective heat-recovery configurations for micro-combustor is constituted to date by the swiss-roll, where the counter-current heat recirculation reactor is coiled up allowing a combustion chamber at its center [108, 110, 111].

Many theoretical studies report that heat recovery strategy is effective in preventing blowout [109, 112]. Compared to a single channel reactor (without heat recirculation), a heat-recovery based reactor allows a strong decrease in the optimum reactor wall thermal conductivity thus involving a much more efficient heat transfer of the power released by combustion towards the cold reactants [104, 110]. It is theoretically found that a more efficient heat transfer in heat recirculation reactors is due to a change in the pre-heating mechanism of incoming gas. As already reported, in a single channel combustor the latter occurs via axial heat transfer through the reactor walls. On the contrary, in a heat recirculation reactor the pre-heating of incoming reactants occurs through transverse heat transfer from countercurrent recirculation gases [106, 112]. However, from theoretical studies, such an enhancement in heat transfer rate is effective only in the limit of low conductive reactor walls. In the case of highly conductive wall, in fact, it is reported that the rate of axial heat transfer through the reactor wall may be faster than that ruled by the transverse thermal gradient [106, 112]. Similar results are obtained in the case of reverse flow reactor; even in this case, in fact, heat recovery is effective only in the limit of low conductivity materials [109].

Theoretical results concerning the effects of heat recovery on combustion stability as well as the effect of wall conductivity are not satisfactorily experimentally validated. Experiments with metallic (stainless steel) heat recirculation reactor have indeed confirmed the marginal improvement in stability with heat recirculation [113]. However, no direct experimental validation exists for low conductive materials, which, in fact, cannot easily be machined thus making the fabrication of micro-reactors extremely difficult.

Another strategy to enlarge the operating window of a micro-combustor is the use of a catalyst. As stated by Fernandez-Pello [102], "*One important aspect of micro-scale combustion that should be* *kept in mind is that although the increase of the surface-to-volume ratio of the combustor presents a problem for gas-phase combustion, it favors catalytic combustion. Although the catalytic reaction is generally slower than the gas-phase reaction, and surface heat loss is a problem that also affects the catalytic reaction, the relative increase of surface area and the lower temperatures of the catalytic reaction suggest that micro-scale combustors using catalytic reaction may be easier to implement than those using gas-phase reactions".* Accordingly, the use of a catalyst allows combustion to occur in a faster and non-inhibited way, also enlarging the range of the process operability and allowing high combustion efficiency even in lean conditions. As a result, catalytic micro-combustion may be sustained at significantly lower temperature compared to its homogeneous counterpart, as suggested by Fernandez-Pello, thus also minimizing concerns as regards materials durability.

Another key aspect favoring catalytic micro-combustion is that the produced heat has to be converted into power through an energy conversion system. A possible approach to convert the chemical energy of the fuels into electricity is to scale gas turbines, characterized by a very high overall efficiency (of about 40%), down to micro-scales. This kind of solution based on thermodynamic cycles has been motivated by the advances in MEMS (Micro Electro-Mechanical Systems), allowing the fabrications of micro-turbines and micro-pumps, and is pursued mainly by MIT (Massachusetts Institute of Technology) [114-115]. However, the hypothetical advantage arising from high theoretical efficiency has to be re-evaluated by considering the lifetime of these kinds of devices. Even if novel fabrication technique allows to scale down power production plants, the friction losses are hardly scalable and component usury strongly reduces the durability of these devices at the micro-scale.

An alternative approach is based on system converting combustion power directly into electricity without including thermal cycles and moving parts. In such a case, conversion system is coupled with combustor constituting a heat source for the process. Several conversion principles have been proposed and among these the most studied are thermoelectric, TE [116-118], and thermophotovoltaic, TPV [119]. Nowadays, TE and TPV exhibit a theoretical efficiency maximum equal to 10%, significantly lower than that of fuel cell and micro-turbine based generators. However, they are characterized by high compactness, operation flexibility, durability, low cost and maintenance. In this context, catalytic combustion appears the best choice because the heat can be produced along the reactor, allowing a better distribution of power released via combustion thus increasing the efficiency of thermal to electrical conversion system [120].

Moreover, catalytic combustors are safer than their homogeneous counterparts and it is commonly reported that the presence of a catalyst inhibits flame [107].

It is trivial that structured catalysts are mandatory for this type of application; moreover, platelet substrates appear to be the best choice for the development of micro-power generators. The development of micro-reactors has been also due to the progress of new deposition techniques that have been applied in order to obtain planar structured catalysts on both metallic and ceramic substrates, such as electron beam deposition [114] and sputtering [121] for active phase deposition and anodic oxidation of aluminum [122] for in situ alumina formation, used as active phase support.

The most common active phase employed in micro-combustion studies is platinum [107, 109, 114, 120-122]. This is not surprising; as a matter of fact, as reported above, the noble metals are the most active phases for combustion and can work at relatively low temperatures. Moreover, for micro-combustion applications the fuels are generally low chain hydrocarbons, especially propane and butane, and/or hydrogen, which show the highest reaction rate on Pt catalysts (only CH_4 reacts faster on Pd than on Pt, as reported in the first part of this paper). As a consequence, on Pt catalysts the different studies have been devoted to the improvement of the thermal management of the reactor, which is crucial in the presence of a catalyst, as well as for homogeneous micro-combustor. In this scenario the most important parameters are the reactor temperature profile, influencing the heat transfer efficiency to the TE or TPV device, and the stability map. Both of them are functions of the thermal conductivity of the micro-combustor walls. As examples, Norton *et al.* [122] verified that the use of copper thermal spreaders is related to a more uniform temperature profile inside the micro-combustor with two beneficial effects: a better heat transfer to an energy conversion device and a reduced peak temperature, related to longer durability of the catalyst. On the other hand, as reported for homogeneous micro-combustor, the stability map of catalytic micro-burners is severely affected by thermal conductivity of the walls [105]. In particular, very low thermal conductivity materials (<1 $W{\cdot}m^{-1}{\cdot}K^{-1}$) allow high fuel conversions only if heat losses are very limited, while too much heat dispersion results if the thermal conductivity is higher than 10 $W{\cdot}m^{-1}{\cdot}K^{-1}$, implying that the best choice is a compromise. Different conclusions have been obtained by Di Benedetto *et al.* [123] who proposed and modeled a new hybrid (catalytic-homogeneous) micro-combustor. In this case, in order to ignite the unburnt fuel exiting the catalytic section inside the microchannel, high thermal conductivity (20 $W{\cdot}m^{-1}{\cdot}K^{-1}$) is necessary.

Another way to manage the heat inside a micro-combustor is the heat recirculation. As a matter of fact, the combustion stability depends on the catalyst temperature that could be increased by heat transfer between reacted and fresh gases, as it occurs in Swiss-roll micro-combustors. The positive effect of heat recirculation on operating window of a micro-combustor has been demonstrated by Scarpa *et al.* [124]. The authors showed that the use of heat recirculation, performed by creating a flow path favoring the heat exchange between reactants and products, can allow the micro-combustor to be operated in a wide range of equivalence ratio. It is trivial that changing the equivalence ratio is the way to control the produced power.

Few cases have been reported in the literature regarding perovskite catalysts and they are generally related to methane micro-combustion. Scarpa *et al.* [21] reported a kinetic study on a micro-combustor with the aim of verifying the effect of hydrogen addition to methane using $LaMnO_3$ as catalyst. Under their experimental conditions, these authors detected a competitive effect of the two fuels, leading to a decrease of combustion reaction rate with respect to the single fuel combustions (Figure 9). On the other hand, at 800°C the occurrence of homogeneous hydrogen ignition, even in a 1 mm combustion chamber, leads to enhanced methane combustion also occurring in the homogeneous phase.

Other studies on the effect of hydrogen addition to methane have been performed under auto-thermal condition on noble metals doped perovskites [10, 125-126].

While under kinetic conditions hydrogen competes with methane to burn on the same sites, as reported above, a positive effect of hydrogen addition to methane has been detected in terms of light off temperature (Figure 10a) over Pt-doped perovskite [125].

The main reason of such effect is due to thermal causes. As a matter of fact, depending on the

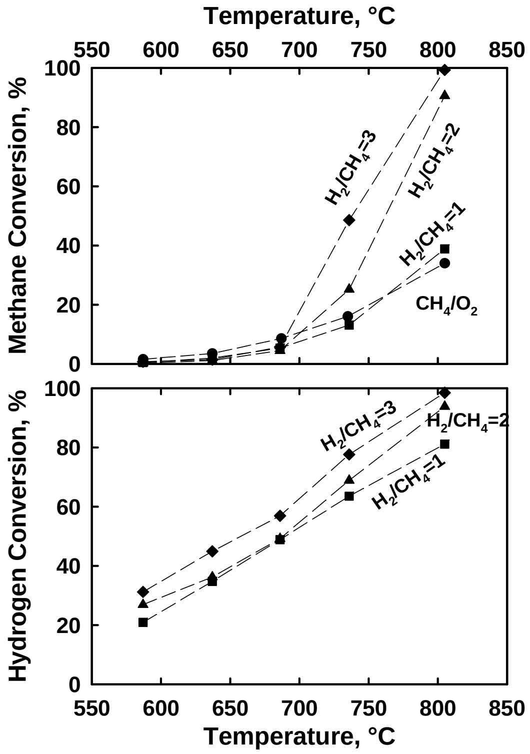

Figure 9. Combustion of CH_4-H_2 mixture over $LaMnO_3$ catalyst (Adapted from [21]).

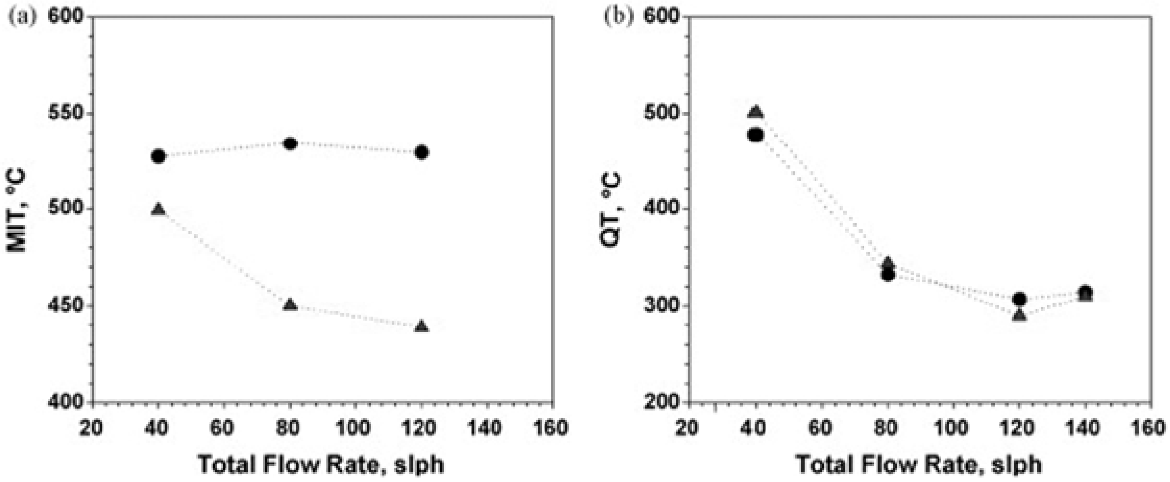

Figure 10. Minimum Ignition Temperature (a) and Quenching Temperature (b) of CH_4 (●) and CH_4–H_2 (▲) combustion as a function of flow rate (Adapted from [125]).

catalyst formulation, hydrogen can be easily converted in the first part of the reactor and the produced heat increases the temperature (and consequently the kinetics) downstream up until the imbalance between generated and exchanged heat is reached. Due to very high hydrogen reactivity over Pt, the bi-functional Pt-perovskite catalysts seem good candidates to perform catalytic combustion of CH_4-H_2 mixtures. The enlargement of the operating window in terms of light off temperature obtained by hydrogen addition is not extendable to quenching conditions (Figure 10b).

This result strongly suggests that quenching phenomena are ruled by the ratio between the developed power via combustion and the power transferred to surroundings via heat losses, independent of the chemical composition of the fuel. As a matter of fact, once the fuel is ignited, the thermal balance, which regulates the self-sustainability of the reactor, exclusively depends on the ratio between the generated power and heat losses, both of them unaffected by fuel composition in these experiments. This behaviour is different from that observed on H_2/CH_4 flames [127-128], where extinction phenomena strongly depend on the hydrogen-to-methane ratio. In fact, under homogeneous conditions H_2 co-feeding influences CH_4 combustion chemistry, while as evidenced before, under catalytic conditions H_2 effect is mainly thermal.

In conclusion, in the field of micro-combustion the catalytic approach seems the most promising, due to the large surface-to-volume ratio typical of micro-reactors. For the same reason heat balance is more demanding in order to achieve stable operation in a wide range of conditions. Except for methane fuelled applications, Pt as active phase seems an obliged choice to date. As a consequence, the most interesting routes in order to enlarge the operating window of a micro-combustor appears related to the heat management or to new concepts such as hybrid micro-burners. On the other hand, especially for methane micro-combustion, hydrogen addition has been revealed as an interesting way in order to reduce light off temperature.

CONCLUSIONS

During the last few years, the interest towards catalytic combustion has been renewed due to the development of new power production scenarios.

Fuel-rich catalytic combustion has been proposed as an alternative staged route to convert natural gas in gas turbine cycles. To date, catalysts are Rh-based, the reduction of noble metal content being the most demanding challenge. Moreover, catalytic performance under operating conditions approaching those of a gas turbine, is significantly influenced by heat transfer along the reactor through both gas-solid and intra-solid heat exchange.

A different approach for power production by gas turbines is related to combustion of syngas-based fuels. In this case, reaction condition should be necessarily fuel-lean and the most investigated active phase is platinum. In the literature some works report experimental tests under pressure, better reproducing gas turbine operating conditions, and the relative model of the reactor behavior in a wide range of operative conditions. Anyway, experimental data appear limited, while two completely different approaches have been used to reproduce them: detailed description of the reaction scheme (thus including more than 50 homogeneous and heterogeneous reactions for H_2 and CO combustion only) and single reaction rates derived from simple models.

While for gas turbine applications catalytic combustion seems a possible alternative, for micro-combustion applications the use of a catalyst appears unavoidable, because of the significant surface-to-volume ratio favoring surface phenomena and heat dissipation. Also in this case, papers have been mainly devoted to platinum catalysts, while the right choice of micro-burner materials appears fundamental in order to obtain a good heat management and, as a consequence, to enlarge the operating window.

From a general point of view, this paper points out that in catalytic combustion applications the development of a suitable catalyst is related to two different aspects. The first is the opportune choice of the active phase, which should be tuned according to some considerations: working temperature (related to deactivation phenomena too), fuel, oxidising or reducing environment, cost, etc. The second is the opportune choice of the substrate in terms of geometrical and physical features, which influences mass and heat transport phenomena occurring not only during steady state operation but also during light off and quenching transients.

Finally, the use of low BTU fuels appears a promising route to catalytically enlarge operating windows of combustion systems. In particular, it has been demonstrated that methane light off occurs at lower pre-heating temperatures, suggesting that an opportune choice of fuel composition could lead to ignition at compressor exit temperature for GT systems.

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