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Facing the catalytic combustion of CH_4/H_2 mixtures into monoliths

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ABSTRACT

Catalytic combustion of methane mixed with hydrogen in micro-scale channels is becoming a key research topic, for various portable power generation devices that could replace current batteries to meet the increasing demand for more efficient, longer lasting and more environmentally friendly energy-consuming utilizations. The present work deals with the investigation on the performance of catalyst 2% Pd over 5% $LaMnO_3 \cdot ZrO_2$ (PLZ), lined on silicon carbide (SC) or cordierite (CD) monoliths, for the CH_4/H_2/air lean mixtures oxidation. The bare and coated monoliths were tested into a lab-microreactor designed to provide a favourable environment for microscale combustion of various CH_4/H_2/air lean mixtures to reach high power density (7.6 $MW_{th}\ m^{-3}$; GHSV 16,000 h^{-1}). The main goal of the catalytic combustion tests was to select the best settings to achieve stable combustion conditions at the lowest possible temperature, i.e., full CH_4 conversion with the minimum H_2 concentration in the reactive mixture, accompanied by the lowest possible CO concentration.

Depending on the thermal conductivity of the tested monoliths, the existence of the steady-state multiplicity was verified, mainly when the H_2 concentration was quite low. Basically, CD monoliths exhibited shorter ignition times compared to SC ones, due to the formation of spatially localized hot spots that promoted catalytic ignition. At the same time, the CD monoliths required shorter times to reach steady-state. But SC materials assured longer time on stream operations. The presence of the catalyst lined on both monoliths allowed reaching lower CO emissions. The best results belonged to the coated SiC monolith, with very low H_2 concentration in the mixtures.

1. Introduction

In the recent years, there are remarkable efforts to progress in the field of microscale combustion, i.e., when employing a combustor characterized by a diameter smaller than approx. 1 mm [1,2]. The main driving force behind these efforts is the much larger energy density obtainable by using commercial fuels when compared with batteries [2,3]. Several works demonstrated the capability of combustion in microscale: some research groups started to build devices that use the microscale combustors or microburners in various applications, as microcomputers or microburners integrated with thermoelectric [4–7] or thermophotovoltaic [8,9] for combined power and energy applications, or micropropulsion [10,11].

During heterogeneous catalytic combustion, the residence time in the burner is a key parameter in determining the rate of species to the solid surface and the adsorption/desorption phenomena on the latter. Since in general the residence time will be small in microcombustors, it is important to have small chemical time scale to ensure completion of the combustion process within the combustor [1]. In general, small chemical time scale are attained by high combustion temperatures; the latter can be achieved by using stoichiometric mixtures, by reducing the heat losses from the combustion chamber, by preventing radical depletion at the wall and using highly energetic fuels. In microscale catalytic assisted combustion, as the combustor size decreases, the attainment of the highest as possible internal surface available for catalyst deposition is a must. The surface increase can be obtained, e.g., by creating small size internal channels. As consequence, the surface-to-volume ratio increases, resulting in increased potential destruction of radical species at the walls and internal heat conduction through the channel walls. These mechanisms will increase the chemical time scale and possibly prevent the onset of the gas-phase combustion reaction or lead to quenching of an ongoing reaction.

Consequently, surface effects (interfacial phenomena [1] and time scaling [1,12]) turn out to be more important, and flame quenching (thermal quenching and radical quenching) becomes a problem [1]. The consequence could be incomplete combustion of fuels. In thermal quenching, flame extinction occurs when the heat of combustion cannot compensate the heat loss to the surrounding environment through the wall; therefore, the wall acts as an enthalpy sink. In addition to the thermal quenching mechanism based on the heat losses, there is another extinction mechanism due to blowout [13,14]. Blowout occurs when a flame gets swept

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out of the reactor at low residence time (i.e., high flow rates). In radical quenching, instead, the free radicals are destroyed and form stable products by undergoing termination reactions at the reactor wall. The latter controls the build-up of free radicals that would lead to explosions. However, the combustion is terminated if all the radicals recombine to form stable species on the walls of a combustor. When the size of the combustor becomes particularly small, the removal of these radical intermediates could disturb the combustion reactions.

Quenching phenomena imply that the combustion slows down and stops propagating towards the wall. The minimal distance between the combustion front and the wall at which the combustion is quenched is called the quenching distance. Such a parameter, which is related to the wall heat flux, is one of the main topics of combustion quenching [15]. Quenching phenomena depend on many parameters concerning both the surface state (temperature, material, geometry) and the burning medium (temperature, pressure, composition, gas-dynamics near the surface, flame stretching). The problem of wall quenching can be reduced or prevented by increasing the wall temperature (the quenching distance is approximately inversely proportional to the square root of the temperature) or equivalently preventing the heat losses from the external wall (adiabatic wall) [1]. Elevated operating temperatures of the combustor walls not only help prevent quenching, but also by reducing the chemical time scale help counterbalance the adverse effect of the small residence time and diffusion time in microcombustors [1].

Miesse et al. [2] performed a series of microcombustion experiments to determine quenching distance employing various wall materials (quartz, stainless steel, copper, yttria-stabilized zirconia, and alumina) at different inside wall temperatures. They concluded that thermal quenching dominates at low temperature (250 °C), whereas the radical quenching plays a dominant role at higher temperature (700 °C).

Kim et al. [16] investigated relative significance of heat loss (thermal quenching) and removal of active radicals at the wall (radical quenching) in stoichiometric combustion of a methane–air mixture. They measured quenching distance with virgin and annealed plates of stainless steel, alumina, and quartz at wall temperature from 100 to 800 °C: the obtained results indicated that the two quenching phenomena were temperature-dependent. At low temperatures, quenching distances were independent of the surface characteristics such as oxygen vacancy, grain boundary, or impurities. At high temperatures, instead, surface characteristics strongly affected the quenching distance.

Miesse et al. [3] studied the homogenous microcombustion of methane and observed a sequence of isolated reaction zone structures (flame cells) along the gas flow path in the microchannel. They summarized the flame stability conditions, obtained for various air stoichiometries ($0.28 < \lambda < 3.4$) and total gas flow rates, giving a map of the observed flame structure regimes.

To achieve combustion in microscale burners, heat recirculation is one possible solution to redistribute thermal energy within a microcombustor and minimizing the heat losses to the outside environment. Kaisare and Vlachos [13] presented a comprehensive study about the effects of reactor dimensions and operating conditions on thermal quenching. They studied the roles of heat recirculation and heat loss on the flame extinction and blowout in microscale (<1 mm) combustion. For instance, stabilization of flame could be achieved by the heat recirculated upstream through the reactor solid structure. Moreover, the heat loss to surroundings had a stronger effect on extinction than on blowout. In addition, Norton and Vlachos [17,18] also found that wall thermal conductivity was vital in determining the flame stability of propane/air and methane/air combustion in microscale. Their two-dimensional elliptic computational fluid dynamics (CFD) model showed that the heat transferred upstream through the walls was beneficial for ignition of the cold incoming fuel-air mixtures but was also responsible for the external heat loss.

Maruta et al. [14] used computational methods to examine the extinction limits for self-sustaining catalytic combustion of methane–air mixtures in microscale channels. The geometry of the microcombustor was chosen so that axial heat conduction and gas-phase reactions could be neglected (very thin wall and very small ID). The study determined the actual temperature profiles for which the microcombustor was self-sustained owing to a balance between the heat release from the surface reaction and the heat loss to the surrounding environment: under adiabatic boundary conditions λ at the extinction limit monotonically increased by increasing the Reynolds number. Thermal extinction was caused by heat loss through the wall. In addition, their results also suggested that with exhaust gas recirculation near-stoichiometric mixtures, rather than the lean ones, are preferable for minimizing flame temperatures in catalytic microcombustors. These findings were also confirmed with another study with propane fuel [19].

CH_4/H_2 mixtures are of great interest nowadays: mixing CH_4 with H_2 might be advantageous due to the higher oxidation reactivity of the latter which could facilitate the burning appliances start-up [20] and/or stabilize the catalytic reaction without the need of further pre-heating [21]. Moreover, the blend of 5–20% of H_2 in CH_4, termed Hythane® [22], is becoming an alternative fuel for CNG vehicles, with advantages in terms of lower CO_2, CO and NO_x emissions. The higher the H_2 percentage, the lower the noxious emissions and the higher the calorific value of the mixture when compared with CNG vehicles. Hythane® can be easily integrated into the existing CNG infrastructure, making it simply and rapidly exploitable in practical applications, not only related to vehicles mobility [23,24], but also for portable applications [25–28].

The present work deals with the investigation on the performance of catalyst 2% Pd over 5% $LaMnO_3 \cdot ZrO_2$ (herein after called PLZ), lined on silicon carbide (herein after called SC) or cordierite (herein after called CD) monoliths, for the CH_4/H_2/air lean mixtures oxidation. The coated monoliths were specifically designed to be inserted in a thermoelectric micro-device, for portable or remote power generation. Anyway, the coupling of the microcombustor with the thermoelectric device is out of the scope of the present study. The coated monoliths were tested into a lab-microreactor designed to provide a favourable environment for microscale combustion of CH_4/H_2/air lean mixtures to reach high power density (up to $20\,MW_{th}\,m^{-3}$). PLZ catalyst was directly lined on the different monoliths via *in situ* Solution Combustion Synthesis (SCS). The carriers' % weights refer to the bare monolith's weight, and the Pd % to the carrier's weight (LZ).

The catalyst was selected in line with earlier investigations on micro-combustion of CH_4/H_2/air lean mixtures [29–32]. The two different kinds of monoliths were considered taking into account their very different thermal conductivities properties, namely 3 and $250\,W\,m^{-1}\,K^{-1}$ at room temperature for CD and SC, respectively [33], to understand the effect of the heat recirculation phenomenon on the micro-combustor performance. The main goal of the catalytic combustion tests was to select the best settings to achieve stable combustion conditions at the lowest possible temperature, i.e., full CH_4 conversion with the minimum H_2 concentration in the reactive mixture, accompanied by the lowest possible CO concentration.

2. Experimental

2.1. Catalyst deposition over monoliths

The *in situ* one-shot SCS technique was used to prepare the coated monoliths investigated in the present study. Such a tech-