Hetero-/homogeneous combustion and stability maps in methane-fueled catalytic microreactors

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Abstract

The hetero-/homogeneous steady combustion and the stability limits of methane-fueled catalytic microreactors (Pt-coated) have been investigated numerically in a 1-mm-gap channel at pressures of 1 and 5 bar. Computations were carried out with a full-elliptic two-dimensional model for the gas- and solid-phases that included elementary heterogeneous and homogeneous chemical reaction schemes, heat conduction in the solid wall, surface radiation heat transfer, and external heat losses. Gas-phase chemistry extended the low-velocity stability limits due to the establishment of strong flames and to an even greater degree the high-velocity blowout limits due to the heat release originating primarily from the incomplete homogeneous oxidation of methane. When considering the same mass throughput, the stable combustion envelope at 5 bar was substantially wider than its 1 bar counterpart due to the increased reactivity of both catalytic and gaseous pathways at elevated pressures. Stable combustion could be sustained with solid thermal conductivities at least as low as 0.1 W/mK, while the stability limits reached their larger extent between 20 and 50 W/mK, a range that covers many practical metallic compounds. The stability limits of catalytic microreactors were wider than those reported for non-catalytic systems. Surface radiation heat transfer greatly impacted the microreactor energy balance and combustion stability. At conditions well-below the stability limits, surface radiation provided an efficient heat loss mechanism that moderated the surface temperatures, whereas close to the limits it could stabilize combustion by transferring heat from the hotter rear of the channel to the colder front. Investigation of smaller confinements has shown that gas-phase combustion could be sustained in catalytic microreactors with gaps as low as 0.3 mm.

1. Introduction

Hydrocarbon-fueled microreactors have received increased attention as energy sources for electrical power generation in portable...
consumer electronics due to their superior energy density compared to that of state-of-the-art lithium batteries [1]. Pure gas-phase combustion of methane can be sustained at the sub-millimeter scale in reactors with appropriately annealed walls that mitigate radical quenching [2]. Moreover, practical configurations such as the mesoscale heat recirculating “Swiss-roll” burner have been shown to stabilize near-stoichiometric propane/air flames for small channel widths of 3.5 mm [3]. Despite the feasibility of micro- and mesoscale gaseous combustors, the associated large surface-to-volume ratios call for heterogeneous fuel conversion. Most recent experimental works have thus focused on hydrocarbon catalytic combustion in a variety of microreactor configurations [4–8]. The preferred catalyst in those studies was platinum.

Key issue in the design and thermal management of microreactors (catalytic or non-catalytic) is the delineation of the regimes where stable combustion can be sustained. The stability of pure gas-phase combustion of methane/air and propane/air mixtures has been investigated numerically [9,10] in channels with sub-millimeter gap sizes and walls without radical quenching. Therein, 2-D CFD simulations with a one-step gaseous reaction used to elucidate the impact of heat transfer mechanisms on the energy management at small scales. In pure catalytic methane combustion over Pt, stability issues were investigated in a 1-mm-gap channel with 2-D simulations [11]: a detailed heterogeneous reaction mechanism was used [12] and the thermally thin wall assumption was invoked (no axial heat conduction in the solid). On the experimental front, extinction limits have been mapped out for non-catalytic and catalytic combustion of propane/air mixtures in a heat recirculating “Swiss-roll” burner [3]. The pressure in all aforementioned studies was atmospheric.

Despite the large surface-to-volume ratios of microreactors, the contribution of gas-phase reactions cannot always be ignored. Typically, microreactors employ low inlet velocities (less than 1 m/s), which result in sufficiently long residence times for the heat-up and gas-phase ignition. Validated heterogeneous and homogeneous kinetics are indispensable inputs in the design of catalytic reactors. To this direction, we have introduced the methodology of in situ spatially resolved measurements of major and minor gas-phase species concentrations over the catalyst boundary layer (using Raman and laser induced fluorescence, respectively) as a direct means to assess the heterogeneous and homogeneous reactivities at operating conditions encompassing a wide range of catalytic systems [13–16]. An appropriate elementary gas-phase reaction scheme has been proposed [16], that reproduces the measured gas-phase combustion characteristics of fuel-lean (<0.5) CH₄/air mixtures over Pt at 1 bar ≤ p ≤ 16 bar. A companion study [14] has further validated the elementary heterogeneous reaction scheme of Deutschmann et al. [17] at the aforementioned pressures and mixture strengths. The importance of suitable hetero-/homogeneous kinetics should not be understated in microreactor studies. For example, the onset of homogeneous ignition requires gas-phase schemes that can accurately capture the ignition delay characteristics in the presence of the catalytic pathway. The flame anchoring position, in turn, impacts the heat transfer mechanisms in the microreactor structure and the associated extinction limits.

The present work undertakes a numerical investigation of hetero-/homogeneous combustion in a methane-fueled microreactor with catalytically active Pt walls. Simulations were carried out with a 2-D full-elliptic model for both the gas- and solid-phases. Elementary hetero-/homogeneous chemical reaction schemes were included along with heat conduction in the walls, surface radiation heat transfer, and external heat losses. The main objectives were to investigate the interplay of hetero-/homogeneous combustion, transport, and heat transfer mechanisms in the microreactor and to delineate combustion stability maps in terms of the underlying parameters.

### 2. Numerical

A full-elliptic 2-D laminar CFD code [18,19] was used to simulate the flow in a plane channel of length \( L = 10 \text{ mm} \), height \( 2b = 1 \text{ mm} \) and wall thickness \( \delta = 0.1 \text{ mm} \) (see Fig. 1). A 2-D approach was also adopted for the heat conduction in the wall (solid thermal conductivity \( k_s \)). External heat losses were imposed at the outer wall surface, according to \( h(T_w - T_\infty) \) with \( h \), a heat transfer coefficient, \( T_w \) the local outer wall surface temperature and \( T_\infty = 298 \text{ K} \). Parametric studies were carried out by varying \( k_s \), \( h \) and the inlet velocity \( U_{\text{IN}} \). Pressures of 1 and 5 bar were examined (the latter being of interest in turbine-based microreactors [20]) and the fuel-to-air equivalence ratio was \( \phi = 0.4 \). The methane/air feed was preheated to 700 or 600 K (necessary to sustain combustion of fuel-lean CH₄/air mixtures over Pt [12]); in practice the preheat...
can be accomplished with heat recirculating microburners [3].

Radiation heat transfer exchange between the discretized catalytic surface elements as well as between each surface element and the reactor inlet and outlet sections was accounted for by the net radiation method for diffuse-gray areas [21]. The inlet, outlet, and channel-element emissivities were all equal and the radiation exchange temperatures for the entry and outlet were equal to the corresponding mean gas temperatures. For the \( k \)th channel surface element, the radiation balance becomes

\[
q_k = \varepsilon \sum_{j=1}^{N+2} F_{k,j} \sigma (T_k^4 - T_j^4) + \sum_{j=1}^{N+2} (1 - \varepsilon) F_{k,j} q_j,
\]

where \( q_k \) is the radiant flux, \( F_{k,j} \) is the configuration factor between the finite areas \( k \) and \( j \), and \( j \) runs over the \( N \) channel elements and the inlet and outlet.

In the bulk of the ensuing computations, the emissivity of all surfaces was constant at \( \varepsilon = 0.6 \). Gas radiative emission and absorption were not considered given the small optical paths and the large nitrogen dilution. Solid-phase radiative boundary conditions were applied at the inlet and outlet vertical wall faces. Further details of the numerical model, along with the 2-D solid treatment have been provided elsewhere [18,19].

The elementary heterogeneous scheme of Deutschmann et al. [17] (24 reactions, 11 surface and 9 gaseous species) was used to describe the oxidation of CH\(_4\) on Pt. The C1/H/O elementary mechanism of Warnatz et al. [22] (26 species, 108 reactions) provided the platform for gas-phase chemistry. The aptness of this mechanism has been demonstrated for \( p \geq 6 \) bar and \( 0.05 \leq \varrho < 0.50 \) [16]. To reproduce homogeneous ignition measurements at the lower pressure range \( 1 \) bar \( \leq p < 6 \) bar, a correction in the kinetic parameters of the chain branching step \( \text{CHO} + \text{M} \Leftrightarrow \text{CO} + \text{H} + \text{M} \) has been proposed [16], which was further supported by recent kinetic measurements [23]. The scheme of Warnatz with the aforementioned modification was valid at \( 1 \) bar \( \leq p \leq 16 \) bar [16], and was thus used in the ensuing simulations. Gaseous and surface thermodynamic data were included in the provided schemes. Mixture-average diffusion, including thermal diffusion for the light species [24], provided the gas-phase transport model. Gas-phase and surface reaction rates were evaluated with CHEMKIN [25] and Surface-CHEMKIN [26], respectively.

An orthogonal staggered mesh of \( 24 \times 84 \) points (in \( y \) and \( x \), respectively) over half the gas-phase domain, with finer spacing towards the entry and the wall, was sufficient to produce a grid-independent solution. The computationally less-intensive solid heat conduction was solved on a \( 20 \times 84 \) grid. Uniform inlet profiles were used for temperature, axial velocity and species mass fractions. No-slip was applied for both velocity components at the gas-wall interface \( (y = b) \) and zero-Neumann conditions were set at the outlet \( (x = L) \) and the plane of symmetry \( (y = 0) \). A combination of mainframe clusters and PCs (equivalent to twenty 2.6-GHz processors) was used and the CPU time per run was \( \sim 10 \) h.

3. Results and discussion

Combustion stability diagrams have been constructed by varying independently the external heat transfer coefficient, the inlet velocity, and the wall thermal conductivity. Figure 2 presents such diagrams for \( k_s = 2 \) W/mK and \( \varepsilon = 0.6 \). Therein, diagrams for \( p = 1 \) and 5 bar at \( T_{IN} = 700 \) K and also for \( p = 5 \) bar at \( T_{IN} = 600 \) K were computed by one-parameter continuation for a given \( U_{IN} \) until the critical extinction heat transfer coefficient was reached. To facilitate the forthcoming comparison of the \( p = 1 \) and 5 bar stability limits at a given mass throughput, two different velocity scales are employed in Fig. 2. The stability limits at large \( U_{IN} \) define blowouts due to insufficient residence times whereas at low \( U_{IN} \) limits are derived from heat-loss-induced extinction.

![Fig. 2. Stability diagrams in terms of critical coefficient \( h \) and inlet velocity \( U_{IN} \): \( p = 5 \) bar (squares: \( T_{IN} = 700 \) K, triangles: \( T_{IN} = 700 \) K without gas-phase chemistry, circles: \( T_{IN} = 600 \) K, crosses: \( T_{IN} = 600 \) K without gas-phase chemistry), \( p = 1 \) bar (filled diamonds: \( T_{IN} = 700 \) K). The stable regimes for the 700 K cases are shown by the shaded areas.]
3.1. Coupling of hetero-/homogeneous combustion and heat transfer mechanisms

Streamwise profiles of the local catalytic and gas-phase methane conversion rates are provided in Fig. 3 for four combinations of \( h \) and \( U_{IN} \) (indicated by points A through D in Fig. 2). Cases A–C are at \( p = 5 \) bar and \( T_{IN} = 700 \) K, and Case D is at \( p = 1 \) bar and \( T_{IN} = 700 \) K. For direct comparisons with the catalytic surface conversion rates, the volumetric gaseous conversion rates have been integrated across the channel half-height in Fig. 3 to provide a conversion rate per unit reactor wall area. The corresponding catalyst surface temperatures are shown in Fig. 4. There is significant gas-phase methane conversion in Case A (Fig. 3a) that leads to the formation of a strong flame as illustrated in Fig. 5, which provides 2-D distributions of temperature, CH\(_4\) and OH mass fractions, and gaseous heat release rate. The flame, indicated by the heat release profile in Fig. 5d, is anchored near the wall at \( x = 2 \) mm, but due to catalytic depletion of methane in the vicinity of the wall (Fig. 5b), the most vigorous heat release occurs at the center of the channel farther downstream between \( x = 3 \) and 4 mm. All the same, the flame temperature at the channel-center is only 16 K higher than the local wall temperature (Fig. 5a). Axial conduction in the solid wall keeps the transverse temperature variation inside the wall to 5 K at \( x = 0 \) (at the channel exit the difference drops to 0.2 K). Therefore, the axial catalyst surface temperatures of Fig. 4 closely reflect the temperature inside the solid. Complete methane conversion (>99.99%) is attained at the reactor exit for all Cases A–D, and the two reaction pathways compete for methane consumption. For the moderate velocity of Cases A–C (\( U_{IN} = 0.3 \) m/s), the relative contribution of the gaseous pathway decreases as the extinction limit is approached (Fig. 3) but it always remains significant and a flame is anchored inside the reactor just prior to extinction.

At higher \( U_{IN} \), the hetero-/homogeneous chemistry coupling becomes more involved. Well-known aspects of this coupling include the promotion of gas-phase reactions due to the catalytically induced exothermicity and the inhibition of gaseous reactions due to near-wall catalytic fuel depletion. In general, the hetero-/homogeneous radical coupling is weak in methane combustion over Pt [14,16]. On the other hand, recent studies [16] have identified chemical coupling routes that are particularly relevant at microreactor conditions. The gas-phase combustion of methane can be roughly described by a two-step process, the incomplete oxidation of CH\(_4\) to CO and the main heat-releasing oxidation of CO to CO\(_2\) [27]. The catalytic pathway is a very efficient sink of homogeneously produced CO due to the high sticking coefficient of this species (0.85 on Pt). By depriving CO from the gas-phase, the catalyst inhibits the onset of homogeneous ignition. Nonetheless, the gas-phase can still provide appreciable methane consumption without full flame formation via the incomplete oxidation of CH\(_4\) to CO. This occurs (for both pressures) at higher \( U_{IN} \) (shorter residence times) over a range of heat transfer coefficients below the critical extinction value that increases with increasing \( U_{IN} \). In Case D (\( p = 1 \) bar), for example, the ratio of the gaseous to the catalytic heat release is 0.10 while the corresponding methane consumption ratio is 0.21 (as illustrated by the heat release rates of the forthcoming Fig. 8 and the methane conversion rates of Fig. 3d) due to the incomplete gas-phase methane oxidation.

The gaseous pathway has been generally neglected in previous catalytic microreactor studies. However, as shown next, gas-phase reac-
tions have significant impact on the microreactor performance under most of the conditions studied. When a flame is anchored in the reactor, the spatial extent of the heat release and methane consumption zones becomes narrower. Figure 3a (gray curve) shows the significant lengthening of the catalytic methane conversion profile when gas-phase reactions are ignored. The localized gaseous heat release is more resilient against external heat losses than the more broadly distributed catalytic reactions. In terms of combustion stability, the presence of the gaseous pathway extends at moderate and low velocities the stability limits mildly. Moreover, the associated higher wall temperatures (as seen in Fig. 4 by the temperature profiles of Case A with and without gaseous reactions) are not endangering the reactor integrity. At higher velocities, the catalytic pathway may not attain complete methane conversion as the extinction limits are approached, due to finite-rate catalytic chemistry effects (although, the mass-transport-limited catalytic conversion always guarantees complete methane consumption for the provided geometry and the velocities within the stable regimes of Fig. 2). In those higher velocity cases, the gaseous pathway has a more profound impact on extending the combustion stability limits by allowing for additional heat release. This is shown by two added stability diagrams in Fig. 2 ($p = 5$ bar, $T_{IN} = 700$ and 600 K), which were computed without gas-phase chemistry.

At $p = 5$ bar and $T_{IN} = 600$ K the stable combustion envelope narrows substantially, particularly in terms of $U_{IN}$ (Fig. 2). It is hence evident that sufficient preheat of the feed is necessary for extended stability in fuel-lean CH$_4$/air microreactor combustion. The stability limits at $p = 1$ bar are much narrower than those at $p = 5$ bar ($T_{IN} = 700$ K), when the same mass throughput ($\rho_{IN}U_{IN}$) is considered. The reason is that both catalytic and gas-phase reactivities decline with decreasing pressure (the former scales as $\sim p^{-0.47}$ [14] and the latter as $\sim p^{-1.0}$ [27]). While Case A (5 bar) lies well-inside the combustion stability diagram of Fig. 2, the corresponding case at $p = 1$ bar ($h = 2$ W/m$^2$K) with the same mass throughput ($U_{IN} = 1.5$ m/s) is just outside the high-velocity extinction limit for the given $h$. Despite the reduced gas-phase reaction rates with lower pressure, the impact of the homogeneous pathway is still significant in defining the (narrower) stable combustion envelope.

### 3.2. Influence of solid thermal conductivity

Stability limits are provided in Fig. 6 for two inlet velocities, $p = 5$ bar and $T_{IN} = 700$ K, in terms of the critical heat transfer coefficient for extinction. For low thermal conductivities ($k_s < 2$ W/mK), the reduced upstream heat transfer hinders catalytic ignition (light-off) and causes blow-out. The stability limits at low $k_s$ are narrower at higher inlet velocities (Fig. 6). In comparison to pure gas-phase combustion studies [9], there is a marked difference at the low $k_s$ behavior, which is discussed qualitatively (since the aforementioned...
tioned work refers to different geometry and operating conditions). In pure gas-phase combustion, the blowout limits extend over a narrower range of $k_s$ (~0.4–0.8 W/mK) and are nearly independent of $h$ (the blowout limit line is almost parallel to the $h$-axis). This is because low $k_s$ reduce the conduction of heat away from the highly localized flame region and maintain moderate wall temperatures such that the external heat losses become less effective in removing heat from the walls. On the other hand, in the catalytic microreactor the distributed heat generation of the heterogeneous pathway provides a larger surface area with high temperatures, which in turn lead to enhanced external heat losses. Therefore, the external heat losses play a pivotal role in determining the stability of catalytic systems at low $k_s$. In addition, catalytic microreactors can achieve stable combustion at lower $k_s$ compared to non-catalytic systems: the stable limits extend to $k_s < 0.1$ W/mK, but in practice there is little interest for such materials.

At higher $k_s$ the extinction limits reach their larger extent for $k_s \approx 20$ W/mK and do not alter appreciably when $k_s$ is increased to 50 W/mK. At low $k_s$ the stability limits are defined by blow-out and hence they are narrower at higher $U_{IN}$ whereas at large $k_s$ the limits are heat-loss-induced and hence are wider at higher $U_{IN}$ (Fig. 6). In contrast, pure gas-phase combustion exhibits a peak at $k_s \approx 5$ W/mK [9] and a further increase to $k_s = 30$ W/mK narrows down considerably the stable regimes. The reason is that in pure gaseous combustion large $k_s$ result in efficient removal of heat from the flame vicinity that eventually causes extinction. Despite the profound differences in the stability limit behavior of catalytic and non-catalytic microreactors, the maximum critical $h$ (~24 W/mK$^2$, Fig. 6) is not very different from that reported in non-catalytic microreactors [9]. From the combustion stability point of view, materials such as FeCr-alloy or Si(SiC) are well-suited for catalytic microreactors (Fig. 6).

3.3. Impact of surface radiation

Thermal radiation heat transfer from the hot catalytic surfaces is usually neglected in microreactor studies. However, it can have a strong impact not only on the stability limits but also on the combustion processes well-inside the stability envelope. In the foregoing analysis a surface emissivity $\varepsilon = 0.6$ was considered (its precise value depends on the type of washcoat, the catalyst loading, the surface treatment, etc.). In Case A, which is located well-below the stability limits, the catalyst surface temperatures are everywhere high (>1200 K, Fig. 4). Detailed energy balance of the solid (similar to that of the following Fig. 8) indicates that radiation is a net heat loss mechanism over the entire length of the catalytic surface because heat is radiated towards the significantly colder entry (700 K). Computed catalyst surface temperatures for Case A are shown in Fig. 7 for different emissivities. The non-radiating ($\varepsilon = 0.0$) simulations indicate a substantially higher surface temperature (by 240 K at the entry and 110 K at the rear of the channel) compared to the $\varepsilon = 0.6$ results. The differences between the $\varepsilon = 0.6$ and 1.0 simulations are less pronounced but still significant (up to 100 K). The foregoing are in qualitative agreement with simulations of longer (aspect ratio of 28) catalytic monolithic channels [28]: therein, increasing $\varepsilon$ from zero to unity caused large temperature drops at the entry (up to 500 K) and also moved the peak wall temperature farther downstream for those conditions where light-off was attained practically at $x \approx 0$ (as in Case A of Fig. 7, see also Fig. 3a). When the inlet and outlet sections were treated as black bodies ($\varepsilon_{IN} = \varepsilon_{OUT} = 1$, as in [28]) the curves of Case A (Fig. 7) differed by less than 50 K for $\varepsilon > 0.6$.

The role of radiation changes drastically as the stability limits are approached. Figure 8 provides (Case D) the energy balance terms for each solid phase slice—length $\Delta x$ and thickness $\delta$—surface heat generation $Q_{cat,gen}$, convection to the gas $Q_{conv}$, net radiation $Q_{rad}$, heat loss $Q_{loss}$ and integrated heat conduction $Q_{cond}$ across the solid thickness $\delta$. The gas-phase heat generation is not related to the solid energy balance and was included in Fig. 8 to facilitate the foregoing discussion of Section 3.1. Note that even close to the stability limit, the heat losses constitute a small (although decisive) part of the total solid energy balance. In Case D the catalyst surface temperatures are low at the entry (<900 K, Fig. 4) such that the radiation heat losses of the front surface elements to the inlet (700 K) are minimal. This leads to a positive net radiative heat flux for the first 2.5 mm and a negative for the remaining length.

![Fig. 7. Surface temperatures of Case A (black solid lines) for three emissivities. The dashed gray lines refer to $k_s = 30$ W/mK (all other parameters being the same with Case A).](image-url)
heat is transferred from the rear of the channel to the front and this has a stabilizing effect on combustion. Computations with non-radiating surfaces for Case D ($\varepsilon = 0.0$) led to extinction of the combustion because upstream radiation heat transfer was necessary for catalyst light-off. The same behavior was also attested in Case C. Finally, at larger $k_s$, the impact of radiation in reducing the entry temperatures becomes less severe (Fig. 7).

3.4. Effect of flow confinement

Additional simulations were carried out for channel half-heights of 0.30 and 0.15 mm. The main interest was to assess whether the homogeneous pathway still plays a role at such increased confinements; the detailed study of those confinements is outside the scope of this work. Computed 2-D distributions of the OH mass fraction and gaseous heat release rate are provided in Fig. 9 for those two confinements; the other operating parameters are the same as in Case A (Fig. 2). It is evident from Fig. 9 that gas-phase combustion can be sustained in catalytic microreactors at the sub-millimeter scale. The gas-phase combustion intensity decreases with increasing confinement (smaller channel height) as seen from the provided absolute OH and heat release magnitudes of Fig. 9. By increasing the confinement, the flames of Fig. 9 move upstream as a result of higher surface temperatures in the first 2 mm. This is an outcome of the decreased radiative heat losses due to the reduction of the geometrical exchange view factors with the colder inlet (700 K).

4. Conclusions

The combustion and heat transfer processes in a catalytic microreactor (length and height of 10 and 1 mm, respectively) coated with Pt and fed with fuel-lean preheated CH$_4$/air mixtures were investigated numerically. A full-elliptic 2-D numerical model was employed that included detailed hetero-/homogeneous chemical reaction schemes and heat transfer mechanisms in the solid. Simulations at 1 and 5 bar have shown that the homogeneous reaction pathway could not be ignored at microreactor-relevant confinements and operating conditions. The presence of the gaseous pathway extended appreciably the blow-out stability limits (high inlet velocity branch) and moderately the extinction limits (low inlet velocity branch). When considering the same mass throughput, the stable combustion envelope at 5 bar was substantially wider than at 1 bar due to the increased reactivities of both catalytic and gas-phase reaction pathways at elevated pressures. Stable combustion could be sustained with solid thermal heat conductivities ($k_s$) at least as low as 0.1 W/mK, while for $k_s$ below 1.0 W/mK the allowable external heat losses became nearly independent of $k_s$. At $k_s$ between 20 and 50 W/mK, a range that covers many metal and metallic/ceramic materials, the allowable heat losses reached their
highest value. Comparison with literature pure gas-phase combustion studies has shown that the stability limits of catalytic microreactors are wider than those of similar non-catalytic devices. Surface radiation heat transfer has a dual role. For conditions far from extinction, surface radiation moderates the wall temperatures by providing a heat loss mechanism to the colder inlet. However, near the stability borders radiation can stabilize combustion by redistributing energy via transfer of heat from the hot rear to the colder front of the channel and aiding the catalyst light-off. Finally, with the coupling to the exothermic surface reactions, gas-phase combustion could be sustained even at sub-millimeter confinements of the catalytic microreactor.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.proci.2006.07.121.

References


Comments

Carlos Fernandez-Pello, UC Berkeley, USA. Is the catalytic reaction intended to induce the gas phase reaction or does it occur unintentionally? Once the gas phase reaction is initiated the catalytic reaction is repressed, thus the conditions at which the gas phase reaction occur are important.

Reply. In contrast to the Catalytically Stabilized Thermal combustion (CST, candidate technology for large gas-turbines) whereby the presence of gaseous combustion is intentional, in microreactor applications the homogeneous combustion is not necessarily intentional but rather comes as an outcome of the suffi-
ciently long residence times needed to initiate and stabilize catalytic reactions and the associated high surface temperatures which reduce significantly the radical quenching distance. However, this is not to say that gas-phase combustion is undesirable: it has been shown that in catalytic systems gas-phase combustion provides appreciably lower CO emissions and nearly complete methane conversion (>99.99%), in comparison to pure catalytic combustion which yields significantly higher emissions ([14] in paper). Another key issue is the low fuel-to-air equivalence ratios, for which combustion can be sustained. For equivalence ratios of 0.4 (used in this study) or lower, it is doubtful if pure gas-phase combustion could be stabilized in non-catalytic burners. Although catalytic reactions are suppressed upon homogeneous ignition, the exothermicity of the heterogeneous pathway is pivotal in providing high enough surface temperatures to facilitate homogeneous ignition of those lean mixtures.

Ruddy Vincent, Imperial College London, UK. Changing the $h$ term corresponds to changing heat loss. For your cases A, B, and C what is sitting on the surface when the catalytic reactions are delayed downstream (Case C)?

Reply. Increasing the external heat loss term, leads to an increased light-off distance as evidenced in the conversion plots of Fig. 3(a, b, c) pertaining to Cases A, B and C of Fig. 2. The increased light-off distance results in a significant drop of the entry surface temperature (Fig. 4), which in turn progressively increases the oxygen surface coverage, $O(s)$, at the expense of the free platinum coverage, $Pt(s)$. This behavior is well-established in ignition studies ([12,18] in paper) and is attributed to the strong temperature dependence of oxygen adsorption on platinum. At sufficiently low surface temperatures, the surface oxygen poisons the catalyst since it inhibits very effectively the adsorption of methane.