Experimental and numerical investigation of hetero-/homogeneous combustion of CO/H₂/O₂/N₂ mixtures over platinum at pressures up to 5 bar

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Abstract

The hetero-/homogeneous combustion of fuel-lean CO/H₂/O₂/N₂ mixtures over platinum is investigated at pressures up to 5 bar, inlet temperatures (T_{IN}) up to 874 K, and a constant CO:H₂ molar ratio of 2:1. Experiments are performed in an optically accessible channel-flow catalytic reactor and involve planar laser induced fluorescence (LIF) of the OH radical for the assessment of homogeneous (gas-phase) ignition and 1-D Raman measurements of major gas-phase species concentrations over the catalyst boundary layer for the evaluation of the heterogeneous (catalytic) processes. Simulations are carried out with an elliptic 2-D model that includes detailed heterogeneous and homogeneous chemical reaction schemes. The predictions reproduce the Raman-measured catalytic CO and H₂ consumption, and it is further shown that for wall temperatures in the range 975 ≤ T_w ≤ 1165 K the heterogeneous pathways of CO and H₂ are largely decoupled. However, for wall temperatures below a limiting value of 710–720 K and for the range of pressures and mixture preheats investigated, CO(s) blockage of the surface inhibits the catalytic conversion of both fuel components. The homogeneous ignition distance is well-reproduced by the model for T_{IN} > 426 K, but it is modestly overpredicted at lower T_{IN}. Possible reasons for these modest differences can be the values of third body efficiencies in the gas-phase reaction mechanism. The sensitivity of homogeneous ignition distance on the catalytic reactions is weak, while the H₂/O₂ subset of the CO/H₂/O₂ gaseous reaction mechanism controls the onset of homogeneous ignition. Pure hydrogen hetero-/homogeneous combustion results in flames established very close to the catalytic walls. However, in the presence of CO the gaseous combustion of hydrogen extends well-inside the channel core, thus allowing homogeneous consumption of H₂ at considerably shorter reactor lengths. Finally, implications of the above findings for the design of syngas-based catalytic reactors for power generation systems are discussed.

Keywords: Hetero-/homogeneous combustion of syngas; Platinum catalyst; In situ Raman and LIF; Homogeneous ignition over platinum; Catalytically stabilized combustion

1. Introduction

Syngas, consisting mainly of CO and H₂, can be produced from a variety of sources including biomass and coal and has recently attracted increased
interest for enhancing the fuel supply security and flexibility in power generation. Moreover, syngas fuels are better suited for forthcoming carbon capture and sequestration (CCS) strategies [1]. Combustion of syngas can also be of interest for natural-gas-fired power plans, as it facilitates post-combustion CO$_2$ capture. Therein, exhaust gas recycle (EGR) is commonly used to increase the CO$_2$ content in the flue gas, thus assisting its subsequent capture [2]. With increasing amounts of EGR, however, the reactivity of the diluted natural gas mixture is reduced, thus compromising combustion stability. An approach to overcome such stability issues is by adding high-hydrogen containing syngas (produced predominantly via catalytic partial oxidation, CPO, of a fraction of the natural gas) into the diluted reactive mixture [3]. Catalytic processes are of interest not only for the production of syngas (CPO) but also for its subsequent conversion using hetero-/homogeneous combustion [4,5].

Due to the interest in gas-turbine syngas combustion, many recent experimental studies were devoted in improving the understanding of homogeneous kinetics of CO/H$_2$ fuels at elevated pressures [6–13]. However, there is a lack of corresponding high-pressure hetero-/homogeneous combustion experiments for CO/H$_2$ or syngas fuels in general. Fundamental combustion experiments of H$_2$/air over platinum in Appel et al. [14] at atmospheric pressure and more recently in Mantzaras et al. [15] at pressures up to 10 bar have clarified the hetero-/homogeneous chemistry coupling and the underlying competition between the two reaction pathways. For syngas fuels, a recent numerical investigation of hetero-/homogenous CO/H$_2$ combustion over platinum was performed at pressures up to 15 bar in [5].

The present study undertakes a combined experimental and numerical investigation of hetero-/homogeneous combustion of fuel-lean CO/H$_2$/O$_2$/N$_2$ mixtures over Pt at pressures up to 5 bar and CO:H$_2$ molar ratio of 2:1 (relevant to coal-derived syngas). Experiments were performed in an optically accessible channel-flow catalytic reactor coated with platinum. The onset of homogeneous ignition was determined with OH planar laser induced fluorescence (LIF), while the catalytic processes were monitored with one-dimensional Raman measurements of major gas-phase species concentrations. The main objectives were to investigate the hetero-/homogeneous chemistry coupling of the two fuel components and to provide validated hetero-/homogeneous reaction schemes over the investigated range of pressures and inlet temperatures.

2. Experimental

2.1. Hetero-/homogeneous combustion facility

A rectangular channel-flow catalytic reactor was mounted inside a cylindrical tank providing the desired pressurization (see Fig. 1, and for details [15,16]). The reactor comprised two horizontal Si(SiC) ceramic plates, 300 mm long (x), 104 mm wide (y), positioned 7 mm apart (z), and two 3-mm-thick vertical quartz windows (Fig. 1). Using plasma vapor deposition, the inner Si(SiC) surfaces were coated first with a 1.5 mm thick non-porous Al$_2$O$_3$ layer and subsequently by a 2.2 mm thick Pt layer. Total and active surface area measurements using Brunauer–Emmet–Teller (BET) Kr-physisorption and CO-chemisorption, respectively, verified the absence of surface porosity [16]. The surface temperature along the x–y symmetry plane was measured by 12 S-type thermocouples (in each plate), embedded 0.9 mm beneath the catalyst surface through holes eroded from the outer Si(SiC) surfaces.

During fuel-lean catalytic combustion of diffusationally imbalanced fuels having Lewis numbers less than unity ($L_e_{112}$ ~ 0.3) superadiabatic surface temperatures are attained at the reactor entry [14,15,17]. In a fashion similar to earlier pure hydrogen studies [14,15], a cooling/heating arrangement was adopted to suppress the high entry surface temperatures driven by the hydrogen fuel component of the syngas and at the same time to balance the heat losses at the reactor rear. To this direction, the front faces of the ceramic plates ($104 \times 7 \text{ mm}^2$) were contacted to a water-cooled metal frame (see Fig. 1), while the reactor length $100 < x < 300 \text{ mm}$ was heated by two resistive coils.

Pressurized bottles supplied O$_2$ and N$_2$, which were electrically preheated and then mixed with H$_2$ and CO in two sequential static mixers. The CO/H$_2$/O$_2$/N$_2$ premixture was directed to the reactor via a 50-mm long inert rectangular honeycomb section ($1 \times 1 \text{ mm}^2$ channels), which yielded a uniform inlet velocity profile. A thermocouple at
the end of the honeycomb monitored the reactor inlet temperature. Optical accessibility from both reactor sides was provided by two 350 mm long and 35 mm thick quartz windows on the high-pressure tank (Fig. 1). Two additional windows, one at the rear flange of the tank (Fig. 1) and the other (not shown in Fig. 1) at the reactor exhaust, provided a counterflow optical access for the LIF experiments.

2.2. Laser diagnostics

The OH-LIF and Raman setups are depicted in Fig. 1. For OH-LIF, the 532-nm beam of an Nd:YAG laser pumped a tunable dye laser (Quantel TDL90 NBP2UV7T3). Its frequency-doubled radiation (285 nm) had a low pulse energy (~0.5 mJ) to avoid saturation of the \( A(v = 1) \rightarrow X(v' = 0) \) transition. The 285 nm beam was transformed into a light sheet, using a cylindrical lens telescope and a 1 mm slit mask, which propagated counterflow along the \( x-y \) symmetry plane (Fig. 1). The fluorescence from both (1–1) and (0–0) OH transitions at 308 and 314 nm, respectively, was collected at 90° through the reactor and tank side-windows with an intensified CCD camera (LaVision Imager Compact HiRes-IRO, 1392 × 1024 pixels). Channel areas of 100 mm × 7 mm were recorded on a 628 × 44 pixel area of the CCD detector chip. The camera was traversed axially to map the 300 mm reactor extent. At each measuring location, 400 images were averaged to increase the signal-to-noise ratio. The LIF signal was calibrated with absorption measurements performed with the 285 nm beam crossing the reactor laterally (\( z \)-direction), as done in previous studies [14,18]. The Raman light source (526.5 nm) was a dedicated frequency-doubled Nd:YLF pulsed laser (Quantronix Darwin Duo) operated at 2 kHz, with a pulse duration and energy of 130 ns and 43 mJ, respectively. The Raman signal-to-noise ratio was thus improved by a factor ~20 compared to earlier setups using the same Nd:YAG laser for both LIF and Raman [15,16]. The Raman signal of 40,000 pulses was integrated on the detector chip when acquiring an image. The 526.5 nm beam was focused into a vertical line (~0.3 mm thick) by an \( f = 150 \) mm cylindrical lens. The focal line spanned the 7 mm channel separation and was offset laterally (\( z = 15 \) mm) to increase the collection angle and minimize thermal beam steering. Two \( f = 300 \) mm lenses collected the scattered light at 50° with respect to the 526.5 nm beam direction and focused it to the entrance slit of a 25 cm spectrograph (Chromex-250i) having an intensified CCD camera (Princeton Instruments PI-MAX1024GIII). Raman data were acquired over the length 10 ≤ \( x \) ≤ 140 mm by traversing a table supporting the sending and collecting optics, including the Nd:YLF laser (see Fig. 1). The measurement accuracy was ±3% for species compositions ≥3% vol. and ±8% for compositions as low as 0.5% vol.; values less than 0.5% vol. could not be accurately resolved. Raman data closer than 0.7 mm to both solid walls were discarded due to low signal-to-noise ratios.

3. Numerical

An elliptic 2-D laminar CFD code was used for the simulations [14,18]. An orthogonal staggered grid of 460 × 120 grid points (\( x \) and \( y \), respectively) was sufficient to produce a grid independent solution. The temperature, axial velocity and species mass fractions were uniform at the reactor inlet. Fitted curves through the 12 (per plate) thermocouple measurements yielded the upper- and lower-wall temperature profiles, which provided the energy boundary conditions at \( y = 0 \) and 7 mm, respectively. No-slip was applied for both velocity components at the channel walls, while zero-Neumann conditions were enforced at \( x = 300 \) mm.

The detailed heterogeneous scheme of Deutschmann et al. [19] (20 reactions, 8 surface and 8 gaseous species) was employed for the oxidation of \( \text{H}_2/\text{CO} \) over Pt, with a surface site density of \( 2.7 \times 10^{-8} \) mol/cm². For gaseous chemistry, the \( \text{CO}/\text{H}_2/\text{O}_2 \) elementary scheme of Li et al. [13] was used (33 reversible reactions and 12 species). This mechanism has been validated against ignition delay and laminar flame speed measurements at pressures of up to 40 bar. Gas-phase and surface reaction rates were evaluated with CHEMKIN [20] and Surface-CHEMKIN [21], respectively. Mixture-average diffusion, including thermal diffusion, was used in conjunction with the CHEMKIN transport database [22].

4. Results and discussion

The experimental conditions (see Table 1) pertain to \( \text{CO}/\text{H}_2/\text{O}_2/\text{N}_2 \) mixtures with inlet temperatures (\( T_{\text{IN}} \)) and pressures up to 874 K and 5 bar, respectively. The nominal equivalence ratio was \( \phi = 0.33 \), but was reduced for the higher \( T_{\text{IN}} \) Cases 5 (1 bar) and 10 (5 bar) so as to avoid autoignition in the fuel mixing section. For the inlet velocities in Table 1, the incoming Reynolds numbers (\( Re_{\text{IN}} \), based on the channel hydraulic diameter) ranged between 1040 and 2680. Nonetheless, turbulent catalytic combustion studies [23] have clearly shown that the strong flow laminarization induced by the hot catalytic walls guarantees laminar conditions at \( Re_{\text{IN}} \) considerably higher than 3000. Comparisons between measured and predicted 2-D OH distributions are illustrated in Fig. 2 for all cases in Table 1. The measured
Table 1
Experimental conditions. $^a$

<table>
<thead>
<tr>
<th>Case</th>
<th>$p$ (bar)</th>
<th>$\varphi$</th>
<th>$\text{H}_2$ (%)</th>
<th>$\text{CO}$ (%)</th>
<th>$\text{O}_2$ (%)</th>
<th>$U_{\text{IN}}$ (m/s)</th>
<th>$T_{\text{IN}}$ (K)</th>
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<td>0.33</td>
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<td>17.3</td>
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<td>0.33</td>
<td>3.8</td>
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<td>17.3</td>
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<td>504</td>
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<tr>
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<td>0.33</td>
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<td>17.6</td>
<td>12.6</td>
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</tr>
<tr>
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<td>1</td>
<td>0.11</td>
<td>1.4</td>
<td>2.7</td>
<td>18.3</td>
<td>15.1</td>
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<td>1.5</td>
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</tr>
<tr>
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<td>3.9</td>
<td>7.8</td>
<td>17.7</td>
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</tr>
<tr>
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<td>17.3</td>
<td>0.6</td>
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<tr>
<td>10</td>
<td>5</td>
<td>0.22</td>
<td>2.7</td>
<td>5.4</td>
<td>18.3</td>
<td>2.6</td>
<td>692</td>
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</tbody>
</table>

$^a$ Inlet species compositions (% vol.). The balance is $\text{N}_2$. 

Fig. 2. (a) LIF-measured and (b) numerically-predicted OH distributions for all cases in Table 1. The arrows provide the location of homogeneous ignition and the color bars the predicted OH (ppmv).
OH maps have been constructed by using overlapping 100 mm long LIF images. The flames in Fig. 2 exhibit modest asymmetries due to small temperature differences between the upper and lower walls (up to 20 K, see wall temperatures in Fig. 3 for six selected cases). The homogeneous ignition position ($x_{ig}$), indicated by arrows in Fig. 2, was defined in both predictions and experiments as the far upstream location where OH reaches 5% of its maximum value inside the reactor.

Three sequential events will be discussed in the next sections: the pre-homogeneous ignition processes ($x < x_{ig}$) wherein catalytic combustion dominates, the hetero-/homogeneous chemistry coupling leading to the onset of homogeneous ignition at $x = x_{ig}$, and finally the post-ignition homogeneous combustion at $x > x_{ig}$.

### 4.1. Heterogeneous combustion

Axial profiles of computed catalytic ($C$) and gaseous ($G$) molar conversion rates for H$_2$ and CO are provided in Fig. 3. The $C$ plots account for both catalytic surfaces, whereas the $G$ plots were constructed by integrating the volumetric gaseous reaction rates over the 7 mm channel height. The predicted homogeneous ignition locations ($x_{ig}$) in Fig. 2 are also shown in Fig. 3, indicating that the rise in OH corresponds to the rise in homogeneous hydrogen conversion $G_{H2}$ (the $G_{CO}$ conversion commences just downstream of $G_{H2}$). As evident in Fig. 3, over the length $x < x_{ig}$, CO and H$_2$ are predominantly converted by the catalytic pathway.

Comparisons between Raman-measured and predicted transverse profiles of H$_2$/H$_2$O/CO/CO$_2$ mole fractions are provided in Fig. 4 for Case 8 (5 bar), at three axial distances $x < x_{ig}$ so as to eliminate contribution of the gaseous pathway to the consumption of H$_2$ and CO. Since for $T_{IN} < 426$ K, there is a modest but systematic overprediction of the homogeneous ignition distance (see Fig. 2 and Table 2), Raman data for Case 8 are provided in Fig. 4 only for axial distances shorter than the measured $x_{ig}$. The catalytic fuel conversion of CO and H$_2$ is transport-limited, as evidenced by the very low predicted mole fractions of these species near both walls ($y = 0$ and 7 mm); the measurements attest the same behavior, despite the lack of Raman data closer than 0.7 mm from both walls. For $377 < T_{IN} < 874$ K (Table 1) and wall temperatures $975 < T_w < 1165$ K pertaining to the induction length $0 < x < x_{ig}$ (see Fig. 3), a transport-limited conversion was attested for all cases in Table 1, at

### Table 2

<table>
<thead>
<tr>
<th>Case</th>
<th>$x_{ig,m}$ (mm)</th>
<th>$x_{ig,p}$ (mm)</th>
<th>$L_{f,m}$ (mm)</th>
<th>$L_{f,p}$ (mm)</th>
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<td>37.6</td>
<td>246.8</td>
<td>192.1</td>
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<tr>
<td>2</td>
<td>7.1</td>
<td>28.5</td>
<td>191.0</td>
<td>187.5</td>
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<td>27.0</td>
<td>115.6</td>
<td>97.6</td>
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<td>9.8</td>
<td>67.5</td>
<td>67.0</td>
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<tr>
<td>5</td>
<td>70.3</td>
<td>78.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>43.7</td>
<td>49.5</td>
<td>120.0</td>
<td>105.0</td>
</tr>
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<td>7</td>
<td>47.2</td>
<td>93.7</td>
<td>–</td>
<td>–</td>
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<tr>
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</tr>
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<td>77.5</td>
<td>77.0</td>
<td>150.0</td>
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</tr>
<tr>
<td>10</td>
<td>80.2</td>
<td>79.6</td>
<td>–</td>
<td>–</td>
</tr>
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</table>

*a* Ignition distances, $x_{ig}$, and flame lengths, $L_f$ (measured: $m$, predicted: $p$). Lengths are provided only for flame shapes that close within the reactor.
least for \( x \geq 10 \) mm where Raman measurements are available.

To investigate the chemistry coupling between the \( H_2 \) and CO catalytic pathways, all cases in Table 1 were recomputed by replacing the incoming CO with a fictitious species CO* that had the same thermodynamic and transport properties as CO but did not participate in any reaction; the same was then repeated by replacing H\(_2\) with a fictitious species H\(_2^\ast\) (studies with fictitious species have been introduced in [5,24]). It was observed that the catalytic conversion \( C_{H2} \) was practically the same for both CO and CO* simulations and that \( C_{CO} \) was again the same for both \( H_2 \) and \( H_2^\ast \) simulations, indicating a minimal heterogeneous chemistry coupling between the two fuel components. However, this behavior drastically changed for wall temperatures lower than a limiting value. Simulations are provided in Fig. 5 for the conditions of Case 2 but with \( T_{IN} = 400 \) K and two constant \( T_w = 700 \) and 800 K. It is clarified that for such modest \( T_{IN} \) and \( T_w \), gaseous chemistry plays no role. For \( T_w = 700 \) K, comparison between the \( C_{H2} \) conversions for CO and CO* simulations indicates that CO largely inhibits the catalytic conversion of \( H_2 \) and, moreover, completely self-inhibits its conversion (Fig. 5a). This inhibition is effectively removed at \( T_w = 800 \) K (Fig. 5b), where the \( C_{H2} \) conversions for both CO and CO* simulations coincide. The origin of this inhibition is clarified with the surface coverage (Fig. 5). At \( T_w = 700 \) K the surface is blocked by CO(s), whereas at \( T_w = 800 \) K O(s) becomes the main coverage and Pt(s) increases by a factor of 10, thus facilitating the adsorption and subsequent oxidation of both \( H_2 \) and CO. Parametric studies over the pressures and inlet temperatures shown in Table 1 indicate that CO(s) surface blocking commences for \( T_w \) below a critical value around 710–720 K. It is worth noting that recent numerical studies of lean CO/H\(_2\) catalytic combustion [5] at much lower CO:H\(_2\) ratios (down to 1:14.5) and pressures up to 15 bar have also shown a similar wall temperature limit (\( \sim 700 \) K) for the CO-induced inhibition.

The implication for power generation systems, whereby inlet temperatures are at least 750 K (in reheat engines they can exceed 900 K [2]), is that syngas catalytic combustion can be accomplished favorably: this is because during start-up the reactor can be preheated by the hot compressed air or the exhaust gas to temperatures well-above 700 K before injection of syngas.

### 4.2. Homogeneous ignition

Detailed comparisons between measured and predicted homogeneous ignition distances (\( x_{ig} \)) are provided in Table 2 for all cases in Table 1. In addition, measured and predicted flame lengths (\( L_f \)), defined as the distance between \( x = x_{ig} \) and the axial location of maximum OH mole fraction on the symmetry plane (\( y = 3.5 \) mm), are compared in Table 2. Flame lengths have not been compared for Cases 5, 7, 10 as the flame shapes do not close and extend down to the reactor exit. The predicted \( x_{ig} \) are in very good agreement with the measured ones for all pressures and \( T_{IN} > 426 \) K (Fig. 2 and Table 2); it is clarified that such inlet temperatures are relevant for gas-turbines. Moreover, for those cases wherein a good agreement between measured and predicted \( x_{ig} \) is established, the corresponding flame lengths are also generally in accord with each other. At \( T_{IN} \) lower than 426 K, \( x_{ig} \) is moderately but systematically overpredicted (Cases 1, 2, 7, 8 in Table 2). Sensitivity analysis has been performed to identify the impact of catalytic and gaseous reactions on homogeneous ignition. Selected cases in Table 1 were recomputed by multiplying and dividing the pre-exponential of each catalytic reaction by a factor of 20 (resulting for certain adsorption reactions to greater-than-unity sticking coefficients); for some reactions the applied factor was lowered to ensure converged solutions.
Hydrogen adsorption (S1) exhibits the largest (negative) sensitivity, but its absolute impact is small since reactions are practically transport-limited (Fig. 4). The S1 sensitivity drops with increasing T\text{IN} (Fig. 6b) due to the corresponding rise of the catalytic reactivity that maintains hydrogen conversion close to the transport limit even after a significant reduction of the S1 rate. The same behavior is also attested with rising pressure: the S1 sensitivity for Case 7 (Fig. 6a) is a factor of three smaller than that of Case 1 (not shown in Fig. 6), due to the increasing catalytic reactivity of H\textsubscript{2} with rising pressure [5]. The CO adsorption/desorption reactions (S15/S16) are also significant, as they control the CO(s) coverage. Finally, radical adsorption/desorption reactions have a much weaker dependence. The good agreement between Raman data and predictions in Fig. 4 indicates that the main species adsorption/desorption reactions are correctly reproduced for the conditions in Table 1, thus removing any uncertainty – small anyway – of catalytic reaction rates on homogeneous ignition.

Sensitivity of homogeneous ignition on gas-phase reactions is provided in Fig. 7. Interestingly, the terminating step H + O\textsubscript{2} + M \rightarrow HO\textsubscript{2} + M, which is controlling the hydrogen homogeneous ignition [14], is not included in the 10 most significant reactions; the same behavior was also reported in CO/H\textsubscript{2} pure homogeneous ignition delay studies (i.e. without the presence of a catalyst) at initial temperatures below 800 K [10]. The onset of homogeneous ignition in Fig. 2 is controlled mainly by the hydrogen chemistry. All cases in Table 1 were recomputed by removing gas-phase CO reactions (but still allowing CO to act as third body in H\textsubscript{2}/O\textsubscript{2} chemistry) and the predicted x\textsubscript{ig} were essentially the same with those in Fig. 2 (see comparisons in Fig. 8a1 and a2). Since the employed gas-phase mechanism has reproduced H\textsubscript{2}/air homogenous ignition over Pt in earlier studies with practically no mixture preheat (T\text{IN} = 310 K) [15], and because Figs. 8a1 and a2 and 7 have shown a small effect of CO gaseous chemistry on x\textsubscript{ig}, the impact of third body efficiencies was examined. When setting the CO and CO\textsubscript{2} efficiencies to unity (from 1.9 and 3.8, respectively) x\textsubscript{ig} reduces modestly, particularly at lower inlet temperatures. It is plausible that third body efficiencies may account for the modest x\textsubscript{ig} deviations at low T\text{IN}; this is further supported by statements in [10] that refinement of third body efficiencies may be necessary for syngas combustion. Nonetheless, it is emphasized that for gas-turbines with T\text{IN} > 700 K, the employed hetero-/homogeneous mechanisms can accurately predict homogeneous ignition and hence be used for detailed reactor design.

### 4.3. Post-ignition combustion

Flame shapes and lengths are generally well-predicted (Fig. 2 and Table 2), while the measured peak OH values (via absorption calibration) are within 20% of the predicted ones. The presence of flames in catalytic combustors with hydrogen-containing fuels is of key importance for reactor thermal management. Computations [14,15] indicate that, for lean combustion of fuels with Lewis numbers less than unity, the flame is confined near the wall and “shields” the catalyst surface from the hydrogen-rich channel core, thus moderating the superadiabatic surface temperatures caused by the catalytic pathway. The confinement of gas-phase hydrogen combustion (without added CO) near the wall is clearly illustrated in Fig. 8a2 and b2 (see also [15]). However, homogeneous combustion of CO/H\textsubscript{2} fuels extends away from the wall (Fig. 8a1 and b1): the nearly...
diffusonally neutral CO combusts farther away from the wall, the ensuing heat release raises the channel core temperature (Fig. 8b1), and this in turn supports gaseous H\textsubscript{2} combustion away from the wall. The end result is that gaseous H\textsubscript{2} conversion can be accomplished at considerably shorter reactor lengths (see Fig. 9) in the presence of CO. This is an important design aspect for practical reactors. It is finally noted that flames during catalytic combustion of H\textsubscript{2}-containing fuels are highly desirable since, apart from the abovementioned moderation of surface temperatures, they also lead to a faster fuel conversion than that attained by catalytic combustion alone (gas-phase combustion does not have the strong transport limitations inherent in the catalytic pathway).

5. Conclusions

The combustion of fuel-lean CO/H\textsubscript{2}/O\textsubscript{2}/N\textsubscript{2} mixtures over Pt was investigated at moderate pressures up to 5 bar and inlet temperatures up to 874 K. In situ, laser-based measurements determined the catalytic CO/H\textsubscript{2} conversion and the onset of homogeneous ignition using Raman and OH-LIF, respectively. Predictions were carried out with a 2-D elliptic model that included detailed hetero-/homogeneous chemical reaction mechanisms. For catalytic wall temperatures 975 \leq T\textsubscript{w} \leq 1165 K, the heterogeneous pathways of CO and H\textsubscript{2} were largely decoupled. However, for $T\textsubscript{w} < 710–720$ K, CO(s) surface blockage inhibited the catalytic conversion of both fuel components. The onset of homogeneous ignition was well-predicted for $T\textsubscript{IN} > 426$ K and modestly overpredicted at lower inlet temperatures, a possible reason for this difference being the values of major species third body efficiencies. The sensitivity of the homogeneous ignition distance on catalytic reactions was particularly weak, while the H\textsubscript{2}/O\textsubscript{2} subset of the CO/H\textsubscript{2}/O\textsubscript{2} gaseous reaction mechanism controlled the onset of homogeneous ignition. Although pure hydrogen hetero-/homogeneous combustion led to flames established very close to the catalytic walls, the presence of CO allowed for the propagation of H\textsubscript{2} gaseous combustion to the channel core, such that homogeneous consumption of H\textsubscript{2} could be achieved at considerably shorter reactor lengths. Implications for the design of syngas-based catalytic reactors for power generation, in terms of heterogeneous conversion and impact of homogeneous combustion on reactor thermal management were finally outlined.

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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.2010.06.135.

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