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Start-up behavior of a $LaMnO_3$ partially coated monolithic combustor at high pressure

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ABSTRACT

In this work, a CFD model was used to investigate the transient behavior of a perovskite-based monolith during catalytic combustion of methane at high pressure. Two configurations were studied, the configuration of a fully coated monolith and that of a partially coated monolith (with only the external channels coated by the catalyst). Simulations were run at different heat transfer coefficients and wall thermal conductivities. The performance of the partially coated monolith was compared to that of the fully coated monolith. Numerical results have shown that, when setting high thermal conductivity and/or high heat transfer coefficient, the partially coated monolith, which provides complete fuel conversion with much lower catalyst load, can operate at low temperature and low ignition time and with reduced cold-start CH_4 emissions.

1. Introduction

Thermal management of catalytic combustors is of crucial relevance [1,2]. Thermal stresses and formation of hot-spots may compromise the integrity of the catalyst, thus reducing the combustor time life [2].

Recently, we proposed a monolith configuration in which the catalyst is removed from the inner channels (i.e., the most adiabatic channels) [3]. We performed CFD simulations of both steady [4] and transient [5] behavior for this partially coated monolith at pressure conditions relevant to gas turbine applications. We showed that the heat transfer through the walls in the radial direction enables activation of the homogeneous reaction in the non-catalytic channels, thus attaining a complete fuel (methane) conversion [4]. We also computed the time evolution of temperature during start-up [5]. We found that the time for start-up is not significantly affected by the partial coating. However, higher temperatures are reached during start-up in the partially coated monolith.

Over the years, several studies on catalytic combustors have been published. The role of the thermal conductivity of the monolith walls [6], the influence of the external heat losses [6,7], the coupling between heterogeneous and homogeneous pathways [4,8,9], as well as the influence of the reaction exothermicity on the velocity profiles [10], have been investigated.

Kaisare et al. [11], by means of a pseudo two-dimensional model of propane catalytic combustion on Pt, pointed out that mass transfer strongly affects the micro-burner performance at low wall conductivities, whereas transverse heat transfer affects stability especially at high wall conductivities.

The few numerical studies focused on the dynamic behavior of catalytic burners are mainly devoted to micro-devices for which fast start-up is highly desirable [12].

Karagiannidis and Mantzaras [13] carried out simulations of the start-up of a methane-fueled Pt-coated micro-burner at different pressures, equivalence ratios and wall thermal conductivities. They found that the increase in both pressure and equivalence ratio positively affects the catalytic reaction rate, thus leading to shorter time to get ignition. A similar behavior has been found in an our previous study [5] when increasing the pressure. Moreover, Karagiannidis and Mantzaras [13] showed that reactors with low thermal conductivity exhibit shorter ignition and steady state times.

Ramanatan et al. [14] modeled the transient behavior of monolithic reactors by means of a one-dimensional two-phase model. They investigated the effect of the wall thermal conductivity on the performance of the monolith. Numerical results have shown that high thermal conductivities are preferable at steady state, but during start-up an increase in transient time and cold-start

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Nomenclature

C_i	concentration of the ith species, kmol/m^3
D	gap distance, μm
d_w	catalytic wall thickness, μm
h_t	exterior convective heat transfer coefficient, W/m^2 K
J_i	flux of the ith species, m/s
L	total length, mm
P, P_i	pressure, atm, partial pressure of the ith species, bar
R	reaction rate, kmol/m^3 s
t	time, s
t_{ig}, t_{igII}	time to get ignition in catalytic channels, time to get ignition in uncoated channels, s
t_{sf}, t_{ss}	time for reaction front propagation, time for steady state, s
T, T_w	gas temperature, wall temperature, K
$T_{w,ext}$, $T_{a,ext}$, T_{in}	temperature at the exterior wall surface, external temperature, inlet temperature, K
v	velocity, m/s

Greek symbols

λ, λ_w	fluid thermal conductivity, solid thermal conductivity, W/m K
ρ	gas density, kg/m^3
ω_h	heat production rate of the surface, J/m^2 s
$\omega_{y,i}$	rate of production/consumption of the ith species, kg/m^2 s

Subscripts

a	ambient
Cat	catalytic
ext	external
Hom	homogeneous
i	ith species
ig	ignition
in	inlet
sf	stable front
ss	steady state
w	wall

emissions is found. Ramanathan et al. [15] derived a light-off criterion to estimate the transient time and cumulative cold-start emissions for a catalytic monolith in the case of non-uniform catalyst loading. They found that, in a monolith with more catalyst near the inlet, cumulative cold-start emissions are substantially reduced.

In this work, we studied the effect of the heat transfer coefficient and the wall thermal conductivity on the transient behavior of a partially coated monolith at high pressure (9.5 bar). This behavior was compared to that of the fully coated configuration in terms of time for ignition and startup, maximum temperature reached during start-up, and steady state and cold-start CH_4 emissions.

2. The model

Details of the two-dimensional CFD model are given elsewhere [5]. Briefly, each channel consists of two parallel (infinitely wide) plates (gap distance, d = 783 μm; catalytic wall thickness, d_w = 45 μm; total length, L = 50 mm). Fig. 1 shows the schemes of the computational domains for the fully coated monolith (Fig. 1a) and the partially coated monolith (Fig. 1b). In this latter configuration, only channels 4 and 5 are catalytically active.

The model solves the transient mass, momentum, chemical species and energy conservation equations in the fluid (coupled to the ideal-gas equation), along with the energy equation in the solid walls.

At the inlet of the channel, fixed flat profiles were assumed for velocity, chemical species and temperature. At the exit, the static pressure was imposed and far-field conditions were specified for the remaining variables.

At the fluid–wall interface, a no-slip boundary condition was assigned (the fluid has zero velocity relative to the boundary) which was coupled to the species balances (the mass flux of each species, ρJ_i, is equal to its rate of production/consumption, $\omega_{y,i}$):

$$\rho J_i = \omega_{y,i} \tag{1}$$

and the energy balance:

$$\lambda \frac{\partial T}{\partial y} = \lambda_w \frac{\partial T_w}{\partial y} + \omega_h \tag{2}$$

where λ is the fluid thermal conductivity, λ_w is the solid thermal conductivity and ω_h is the heat production rate of the surface.

Heat losses from the ends of the channels were not considered (insulated ends), while Newton's law of convection was used at the outer surface of the external channels:

$$q = h_t(T_{w,ext} - T_{a,ext}) \tag{3}$$

where h_t is the exterior convective heat transfer coefficient, $T_{w,ext}$ is the temperature at the exterior wall surface, and $T_{a,ext}$ is the external temperature (assumed as equal to the inlet temperature).

The reaction rate for homogenous methane combustion was calculated according to the single-step reaction rate by Westbrook and Dryer [16]:

$$R_{\mathrm{Hom}} = 2.119E+11 \cdot \exp\left(\frac{-2.027E+8}{\Re T}\right) \cdot \left(C_{CH_4}\right)^{0.2}\left(C_{O_2}\right)^{1.3} [\mathrm{kmol/m^3 s}] \tag{4}$$

where the activation energy is in J/kmol, the concentrations in kmol/m^3 and the pre-exponential factor in (m^3/kmol)$^{0.5}$/s.

The reaction rate over $LaMnO_3$/La-γ-Al_2O_3 catalyst used is reported in [17]:

$$R_{Cat} = \frac{3.8 k_1 k_2 P_{CH_4} P_{O_2}}{k_1 P_{O_2} + 2 k_2 P_{CH_4}} [\mathrm{kmol/m^2 s}] \tag{5}$$

The model equations were discretized using a finite volume formulation on a structured non-uniform mesh. The spatial discretization of the model equations used second order schemes for all terms. The time integration was performed by using the second-order implicit Crank-Nicholson scheme. Computations were performed by means of the ANSYS FLUENT code (release 13.0) [18].

Five cases were studied (Table 1): cases 1–3 for the effect of the wall thermal conductivity, λ_w; cases 1, 4–5 for the effect of the external heat transfer coefficient, h_t. In this work, the inlet gas velocity (v_{in}) and temperature (T_{in}), the external temperature ($T_{a,ext}$) and the static pressure at the exit (P_{out}) are constant (Table 1).

3. Results and discussion

In a previous paper [5], we showed the transient behavior of both monolith configurations as computed when setting λ_w = 3 W/m K (cordierite) and h_t = 20 W/m^2 K (case 1 of Table 1 – reference case). We showed that start-up occurs through three phases: phase I – ignition phase, phase II – phase of moving front and phase III – phase of complete development of profiles. Each phase is characterized by different times. The time of the ignition phase (t_{ig}) is the time required to observe the first local hot spot. The time of