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Transient numerical modeling of catalytic channels using a quasi-steady gas phase

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HIGHLIGHTS

- A transient catalytic combustion model for micro channels is formulated and solved.
- The model includes a transient solid, quasi-steady gas, and detailed chemistry.
- The model shows both kinetically and mass-transfer controlled regimes.
- The model compares well to two experiments using CO and O_2 in a Pt tube.
- Sensitivity studies show the effects of transfer coefficients and other parameters.

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ABSTRACT

This paper presents a transient model of internal catalytic combustion suitable for isolated channels and monolith reactors. Due to time-scales in the problem, the model considers a quasi-steady gas phase with a transient solid. The gas is described by axially varying bulk temperature and species. The gas includes lateral diffusion *via* transfer coefficients and the specification of a gas-phase species concentration at the wall; axial diffusion is neglected. The solid phase is a thermally thin shell with axially varying temperature, surface species, and surface species concentrations. The solid includes axial heat conduction and external heat loss by convection and radiation. The combustion process utilizes detailed gas and surface reaction models. The gas-phase model becomes a system of stiff ordinary differential equations with respect to axial position; the upstream (inlet) boundary conditions are specified and the axially varying solid properties are parameters in integration. The solid phase discretizes into a system of stiff ordinary differential-algebraic equations with respect to time. The time evolution of the system comes from alternating integrations of the quasi-steady gas phase and transient solid.

The model is compared to two experimental cases using CO fuel: (1) steady-state conversion in an isothermal platinum tube and (2) transient propagation of a catalytic reaction inside a small platinum tube and includes external tube temperature measurements. This work presents sensitivity studies on important parameters including internal transfer coefficients, catalytic surface site density, external heat-loss, and others. Under mass-transfer limited conditions, global transfer coefficients are adequate to predict fuel conversion. Near light-off, the model predictions improve for the first case after adjusting the surface kinetics such that the net rate of CO adsorption increases compared to O_2. For the second case, predictions of transient propagation speeds are good for equivalence ratios near unity and greater but require adjustment of external heat loss or kinetics to match under lean conditions.

1. Introduction

Catalytic combustion has been extensively studied over the past several decades largely because it offers lower ignition temperatures, can reduce pollutants, and operates with a wide range of fuels and fuel-to-air ratios. While many practical applications exist using catalytic combustion, there still are many aspects where fundamentals are not completely understood. Among active areas of research are the physical surface chemistry (Gélin and Primet, 2002), development of surface kinetic mechanisms (Warnatz et al., 1994; Bond et al., 1996; Deutschmann et al., 1996), physical model development (Kolaczkowski, 1999), and numerical simulations

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(Hayes and Kolaczkowski, 1997; Westbrook et al., 2005). This includes understanding the transient behavior, particularly "light-off" which is of high importance for many catalytic systems that routinely start and stop or see transient inlet feed conditions. Moreover, surface reactions can stabilize homogeneous combustion on scales smaller than the quenching distance (Zamashchikov, 2000; Maruta et al., 2004, 2005; Mellish et al., 2005; Yuasa et al., 2005; Kim et al., 2006; Miller et al., 2006; Struk et al., 2006).

Predicting transient phenomena in combustion, especially ignition and extinction, requires accurate knowledge of the chemical kinetics. Detailed homogeneous chemical mechanisms are prevalent in the literature while heterogeneous chemical mechanisms are becoming increasingly available. Currently, there are significant efforts (Deutschmann et al., 1994, 1996; Reinke et al., 2004, 2005; Appel et al., 2005) in validation of such mechanisms and their inclusion into existing models offers the potential for far better understanding of complex phenomena such as catalytic light-off.

A rigorous physical model of a transient catalytic combustion system can be computationally expensive even without the inclusion of detailed or full chemistry. Thus, models of catalytic monolith reactors simulate a single (or just a few) channel(s) to characterize the behavior of the entire reactor. Despite this reduced geometry, detailed flow treatment can require 3D codes because the channel cross-sections can be non-circular. While some studies in catalytic combustion have begun to couple both multi-dimensional flow fields with detailed homogeneous and heterogeneous chemistry (Zheng et al., 2014; Schwiedernoch et al., 2002; Zheng and Mantzaras, 2014), studies using simplified flow fields with the inclusion of detailed chemistry should not be overlooked. Such an approach was undertaken by T'ien (1981b) and later by Jackson and co-workers who developed a 1D (axial) transient reactor model (Zhu and Jackson, 2001; Kramer et al., 2002).

While there are conditions where plug-flow models (Larson, 1996; Kee et al., 2003) are valid (Raja et al., 2000), many catalytic combustion systems are mass-transport limited and thus require the inclusion of finite rate species transport (Larson, 1996; Raja et al., 2000). There exists an extensive body of literature using simplified chemistry in which catalytic combustion systems have been modeled using simplified flow-fields, *i.e.* the so-called "lumped" models, which capture finite rate diffusion perpendicular to the main flow direction through the use of heat- and mass-transfer coefficients (Ablow and Wise, 1979; T'ien, 1981a; Oh and Cavendish, 1982; Groppi et al., 1995; Hayes and Kolaczkowski, 1997; Gupta and Balakotaiah, 2001; Ramanathan et al., 2003; Kaisare et al., 2008, 2009; Ramanathan and Sharma, 2011). These models, which are less expensive computationally, have successfully predicted a wide variety of catalytic systems but hinge to various degrees on knowledge of accurate heat- and mass-transport coefficients. There have been several studies which explore the use of heat- and mass-transport coefficients in catalytic systems (Ullah et al., 1992; Hayes and Kolaczkowski, 1994; Groppi et al., 1995; Gupta and Balakotaiah, 2001; West et al., 2003; Kaisare et al., 2008, 2009; Joshi et al., 2009; Joshi et al., 2010). A logical next step, undertaken recently, is to include detailed chemistry in a "lumped" catalytic model (Zhu and Jackson, 2001; Kramer et al., 2002).

Finally, many studies have shown that heat conduction along the solid structure of the reactor (Ramanathan and Sharma, 2011) as well as radiant heat transfer (Eigenberger, 1972; Lee and Aris, 1977; Sinkule and Hlaváček, 1978; Hayes et al., 1992; Worth et al., 1996; Boehman, 1998; Ramanathan et al., 2003) can be important. Recently, a catalytic reaction front has been observed to propagate along an isolated Pt channel due to solid-phase axial conduction (Miller et al., 2006, 2007; Struk et al., 2006). For such a configuration, a catalytic combustor model requires the inclusion of conductive heat transfer along the solid as well as upstream solid-to-solid radiative heat transfer. Previous studies have suggested that the primary effects of radiative exchange is to smooth temperature profiles and to advance the light-off position upstream (Boehman, 1998) with axial conduction being more significant (Hayes et al., 1992). For the present study, internal radiation transfer is neglected.

The goal of this work was to develop a two-phase (gas and solid) transient catalytic combustor model using a simplified flow field inside a single channel with axial heat conduction and detailed chemistry. While such models have previously been developed using global kinetics (Oh and Cavendish, 1982; Ramanathan and Sharma, 2011), there are only few studies which include detail chemistry (Zhu and Jackson, 2001; Kramer et al., 2002) with the majority preferring detailed flow-fields. This work explores the advantages and limitations of a simplified flow field model with detailed chemistry by comparing predictions to two separate experiments using CO fuel ($CO/N_2/O_2$ mixture) in a Pt channel: (1) steady-state catalytic oxidation in an isothermal channel and (2) transient catalytic oxidation propagating along a channel. The first case uses data taken from the literature. The second case uses recent experimental data obtained in a pure Pt channel taken by NASA (Miller et al., 2006; Struk et al., 2006). In both of these experiments, the important reactions are heterogeneous, but the model includes homogenous reactions in anticipation of future studies.

2. Model description

2.1. Overview

The model is of an isolated channel of arbitrary cross-section and considers both the gas and solid phase. For the gas, a mixture of fuel, oxidizer, and optional inert enters the channel with a prescribed velocity and pressure. There is negligible pressure drop along the channel and the gas obeys the ideal gas law. The gas phase is quasi-steady relative to the transient solid owing to the significantly longer heat-up times of the solid ($\sim$s) compared with the time constants of gas-phase processes ($\sim$ms). The model uses three different values to describe the constituent species at a given axial location: a bulk gas-phase mass-fraction (Y_k), a mass-fraction adjacent to the wall but still in the gas-phase (Y_{kW}), and chemisorbed species on the surface (Z_k). The bulk and wall species provide an estimate for the gradients so that lateral mass transport can be captured in the gas (*i.e.* a two-layer gas-phase model). The lateral diffusion rate is quantified *via* heat- and mass-transfer coefficients. Heat and mass diffusion in the axial direction is neglected because the Peclet number based on typical gas velocities is much greater than unity. The model uses detailed kinetic mechanisms for both the gas and surface reactions. Transport properties calculations use the bulk temperature and mass fraction of the K_g gas species at each axial location. Inlet boundary conditions are specified for T and Y_k as well as dT/dx and dY_k/dx.

The transient, thermally-thin solid includes heat transfer to and from the gas inside the tube, external heat transfer to the surroundings *via* convection and radiation, heat generation terms due to catalytic reactions and resistive heating (to simulate applied heat), and axial heat conduction. Here, thermally-thin implies infinitely fast heat conduction in the radial direction. The model accounts for varying coverage of adsorbed surface species along the inner surface of the channel adjacent to the gas phase. The amount of adsorbed species is assumed to be sufficiently small so as not to affect bulk material properties. There are K_S total surface species including vacant surface sites. Initial conditions must be specified for Ts, Y_{kW}, Z_k as well as their gradients with respect to time.