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Transient three-dimensional simulations of a catalytic combustion monolith using detailed models for heterogeneous and homogeneous reactions and transport phenomena

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Abstract

The application of a newly developed computational tool, DETCHEM^{MONOLITH}, for the transient two- and three-dimensional simulation of catalytic combustion monoliths is presented. The simulation is based on the coupling of a transient 2D/3D heat balance of the solid monolith structure with steady-state calculations of the reactive flow in a representative number of channels. The two-dimensional single-channel model uses a boundary-layer approximation including detailed models for heterogeneous and homogeneous reactions as well as transport phenomena. As an example, the computational tool is applied to study the hydrogen-assisted catalytic combustion of methane in a platinum-coated honeycomb monolith.

Keywords: Three-dimensional simulation; Catalytic combustion monolith; Heterogeneous and homogeneous reactions

1. Introduction

Monolithic catalysts play an important role in various applications such as automotive catalytic converters [1], large-scale facilities for natural gas conversion [2] and catalytic combustion [3,4]. These systems have received widespread experimental and theoretical attention due to environmental issues and the potential of producing useful chemicals with a reduced consumption of resources. In comparison with experiments, a detailed simulation of the underlying processes will help to verify the theoretical models. Moreover, the simulation becomes an efficient tool in the analysis of the transient flow and thermal phenomena within the catalyst. The results then can be used to design more efficient systems.

In recent years, several proposals have been made for the numerical simulation of monolithic catalysts. Koltsakis et al. [5] used a global model for the catalytic chemical reaction and a plug flow model for the single-channel flows in order to solve a two-dimensional transient heat conduction equation for the monolithic structure. Elementary-step reaction mechanisms for surface and gas phase chemistry and a detailed transport model have been applied for the simulation of flow fields inside single channels of monolithic catalysts used for catalytic partial oxidation of methane [6] and ethane [7]. However, the

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numerical solution of the full Navier–Stokes equations coupled with complex chemistry models is computationally very expensive because the chemistry contributes to the stiffness of the equation system. Therefore, a simulation of the transient behavior of the entire catalytic monolith using detailed models for chemistry and transport has not yet been realized.

Raja et al. [8] evaluated the application of a plug flow model, a boundary-layer model, and a Navier–Stokes model for catalytic combustion monoliths. In their study, it was shown that for a wide range of problems from moderate to high Reynolds numbers, the boundary-layer model is sufficient to describe a single channel, while the plug flow model fails [8]. Several applications of catalytic monoliths are designed for high space velocities, and particularly at those conditions the boundary-layer model appears to be appropriate. Furthermore, the residence time of the reactive mixture in the monolithic channel can often be assumed to be small in comparison with the variations in the thermal state of the solid monolithic structure. Therefore, the simulation of the reactive flow in the single channels and the thermal variations of the monolithic catalyst can partly be decoupled.

In this work, we focus on those spatially structured monolithic catalysts, where the time scales of variations in the gas phase are much smaller than those of the thermal changes in the monolithic structure. Then, the flow through the single monolith channels, which are assumed to have a cylindrical shape, is modeled by a two-dimensional boundary-layer approach with elementary-step gas phase and surface reaction mechanisms as well as a detailed description of the transport properties. The spatial structure of the monolith enables us to set up a three-dimensional model for the heat transport in the solid monolith, which is coupled to the reactive flow by enthalpy source terms derived from the simulation of a representative number of single channels. The developed computer code, named DETCHEM$^{\mathrm{MONOLITH}}$, for the first time offers the possibility of performing transient 2D and 3D monolith calculations using such detailed models for transport and chemistry in the individual channels.

As an example, we present a numerical simulation of the hydrogen-assisted oxidation of methane in platinum-coated honeycomb monoliths. The predicted temperature and conversion are compared with experimental data presented in a previous study [9].

2. Modeling method

The numerical model for the simulation of the monolith is set up in two steps. Since the time scales of the reactive channel flows and of the solid's thermal response are decoupled, time variations in the local monolith temperature can be neglected when calculating the fluid flow through a single channel. Thus, a time-independent formulation is used to describe the gaseous flow in order to calculate heat source terms for a transient heat conduction equation for the solid.

Every channel is modeled using cylindrical symmetry. Given the inlet (velocity, temperature, density, species mass fractions) and wall conditions (temperature), the two-dimensional flow field of the fluid can be solved for.

The set of Navier–Stokes equations is the most accurate model for the description of the laminar flow of a chemically reacting fluid. However, due to their mathematical structure — in the time-independent formulation they resemble a set of nonlinear elliptical partial differential equations — and their stiffness, a numerical solution is computationally expensive [6,8]. Therefore, simpler models such as plug-flug or boundary-layer models [10,11] are frequently used.

In the boundary layer of a fluid near the surface, the convection is mainly directed parallel to the surface. The diffusive transport in the same direction diminishes in comparison with the one perpendicular to the surface. This effect becomes more significant as the axial gas velocity is increased, i.e. for higher Reynolds numbers as long as the flow is laminar. Mathematically, the character of the equations changes from elliptical to parabolic with a time-like coordinate along the channel axis. The set of equations consists of conservation equations for:

Total mass

$$\frac{\partial(r\rho u)}{\partial z} + \frac{\partial(r\rho v)}{\partial r} = 0, \tag{1}$$

Mass of species s

$$\frac{\partial(r\rho u Y_s)}{\partial z} + \frac{\partial(r\rho v Y_s)}{\partial r} = -\frac{\partial}{\partial r}(r j_s) + r\dot{\omega}_s, \tag{2}$$

Axial momentum

$$\frac{\partial(r\rho u^2)}{\partial z} + \frac{\partial(r\rho u v)}{\partial r} = -r\frac{\partial p}{\partial z} + \frac{\partial}{\partial r}\left(\mu r \frac{\partial u}{\partial r}\right), \tag{3}$$

Enthalpy

$$\frac{\partial(r\rho uh)}{\partial z} + \frac{\partial(r\rho vh)}{\partial r} = ru\frac{\partial p}{\partial z} + \frac{\partial}{\partial r}\left(\lambda r \frac{\partial T}{\partial r}\right) - \frac{\partial}{\partial r}\left(\sum_s r j_s h_s\right). \quad (4)$$

As a consequence of the boundary-layer assumption, the radial momentum equation is reduced to the statement that there is no pressure gradient in radial direction.

Given the inlet conditions, the boundary-layer equations are solved in a single sweep of integrations along the axial direction by a method-of-lines procedure. The radial derivatives are discretized by a finite-volume method. The resulting differential-algebraic equation system is integrated using the semi-implicit extrapolation solver LIMEX [12]. The transport coefficients for radial diffusion (μ, λ) and the species diffusion flux j_s depend on temperature and species composition. Surface and gas phase reaction source terms, $j_{s,\mathrm{surf}}$ and $\dot{\omega}_s$, are modeled by elementary-step based reaction mechanisms using the DETCHEM computer package [13]. The model of the catalytic reactions on the inner channel wall accounts for a varying surface coverage of adsorbed species along the channel. Furthermore, a model for pore diffusion inside washcoats, which also depends on the local reaction rates, has recently been developed by Chatterjee and coworkers [14] and can be included when necessary.

The simulation of the thermal behavior of the whole monolithic structure, which is coupled with the single-channel simulations, is modeled by a two- or three-dimensional temperature equation

$$\frac{\partial T}{\partial t} = \nabla^2\left(\frac{\lambda T}{\rho C_p}\right) + \frac{q}{\rho C_p}. \quad (5)$$

The material properties (density ρ, heat capacity C_p and thermal conductivity λ) are functions of the local temperature and material and can also be specified as functions of the direction. Heat losses due to conduction, convection, and thermal radiation at the exterior walls of the monolith can be included. In order to obtain the source terms q in the temperature equation, the heat flux from the gas phase into the monolith bulk due to convection and chemical reactions is calculated for a representative number of channels. These single-channel simulations are carried out for each time step of the transient temperature simulation. They apply the actual local axial temperature profiles as boundary conditions and use the time-dependent initial flow conditions. Hence, time-varying inlet conditions can be specified as long as the conditions vary at a time scale that is larger than the residence time.

For the spatial discretization of the transient temperature equation, a finite-volume approach is used. The resulting ordinary differential equation system can be solved with a stiff-stable integrator, such as LIMEX. Based on these models, the computational tool predicts the transient, two- or three-dimensional distributions of temperature and species concentrations.

3. Application

Much attention has already been drawn to the catalytic combustion of methane, the primary natural gas component, on platinum surfaces. The application of catalytic combustion in gas turbine technology also depends on the feasibility of a convenient light-off mechanism, because ignition of methane on platinum and other noble metals used for catalytic combustion occurs at relatively high temperatures at lean conditions [15,16]. In order to reduce the light-off temperature, some hydrogen can be added to the initial mixture, since catalytic hydrogen combustion ignites at almost room temperature.

In a previous study [9], hydrogen-assisted catalytic combustion of methane on platinum was investigated experimentally and numerically. In the laboratory-scale experiment, a honeycomb monolith was used, being 5 cm in diameter and having a total length of 5 cm. The monolith consisted of a cordierite substrate with an alumina washcoat, in which the platinum was embedded. The surface consisted of 200 honeycomb-shaped cells per square inch, resulting in a diameter of approximately 1.8 mm per channel. The experiment started with a hydrogen–air mixture to be ignited catalytically. Due to the chemical reaction, the monolith's temperature quickly increased. After a steady state was reached, methane flow was gradually increased until light-off of the methane combustion was observed. The outlet temperature was measured using a thermocouple. The reactive flow in a single-channel of the monolith was modeled

by the two-dimensional Navier–Stokes equations which were coupled with a detailed surface reaction mechanism. The numerical simulation of the steady state of the ignited methane/hydrogen/air mixture was based on the commercial CFD code FLUENT which was coupled with external subroutines to model the chemistry [13]. For further reading, we refer to the original literature [9].

With our newly developed computational tool, this experiment was now simulated numerically. First, a two-dimensional description of the cylindrical-shaped monolith with the axial and radial coordinates as independent spatial variables was used. The chemical reactions on the catalytic platinum surface were modeled using 27 irreversible chemical reactions among nine gas phase species and 10 surface species [15]. Homogeneous combustion chemistry in the gas phase was modeled by a set of 344 irreversible reactions among 37 species. This homogeneous reaction scheme is based on a reduction of a large set of hydrocarbon oxidation reactions [17,18] to C_1 and C_2 species. Comparing simulations with and without gas phase chemistry, it was concluded that gas phase reactions can be neglected under the conditions studied.

Beginning with inlet conditions of 5 vol.% hydrogen mixed with air at 300 K and a gas velocity of 0.8 m/s, the steady-state temperature field was calculated. The simulation predicted a gas temperature of 680 K at the outlet with nearly all hydrogen in most of the channels consumed. Because there was some heat loss at the exterior boundary of the monolith in the experiment leading to an exit temperature which is approximately 100 K less than the adiabatic temperature, external heat loss by conduction and thermal radiation was included in the simulation. The heat loss was chosen in a way that the predicted exit temperature matches the measured one.

Starting with the temperature field of the preheated monolith, methane was added to the inflow gas mixture stepwise by increments of 1 vol.% methane. Through transient simulations, the variations in the temperature and species distributions were predicted. Fig. 1 shows the time development of the outlet gas composition and temperature averaged for the whole monolith when the methane feed is increased from 2 to 3%. As the temperature of the monolith rises, more methane is converted into carbon dioxide and water, although it takes about 25 s until light-off occurs.

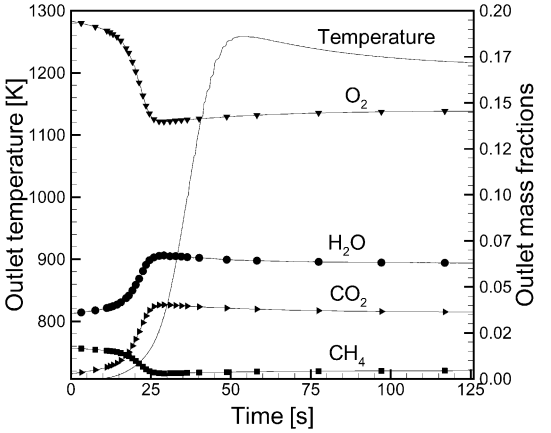

Fig. 1. Variation of outlet temperature and species composition after increasing the methane feed from 2 to 3 vol.% (hydrogen 5%).

The steady-state temperatures and methane conversion as function of methane feed are shown in Fig. 2. In agreement with the experiment [9], almost no methane is burnt while adding only 2% methane or less. According to the simulation, the reaction rate is sufficiently high for light-off of catalytic methane combustion at 3% methane feed. In the experiment, ignition was observed at 3.7%. This difference can be caused by uncertainties left in the thermal properties of the materials used, catalyst loading, and flow maldistribution.

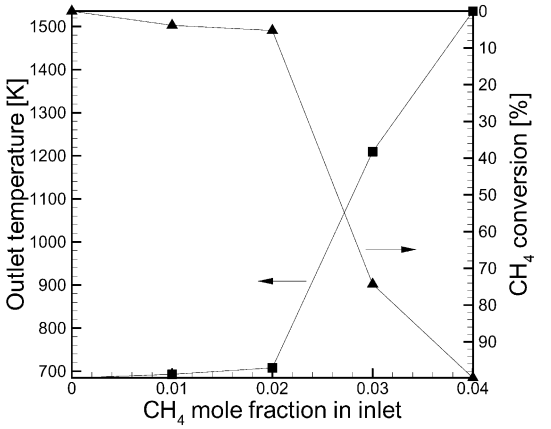

Fig. 2. Outlet gas temperature and methane conversion versus increasing methane feed in air with addition of 5 vol.% hydrogen. The gas enters the catalyst with 0.8 m/s at 300 K.

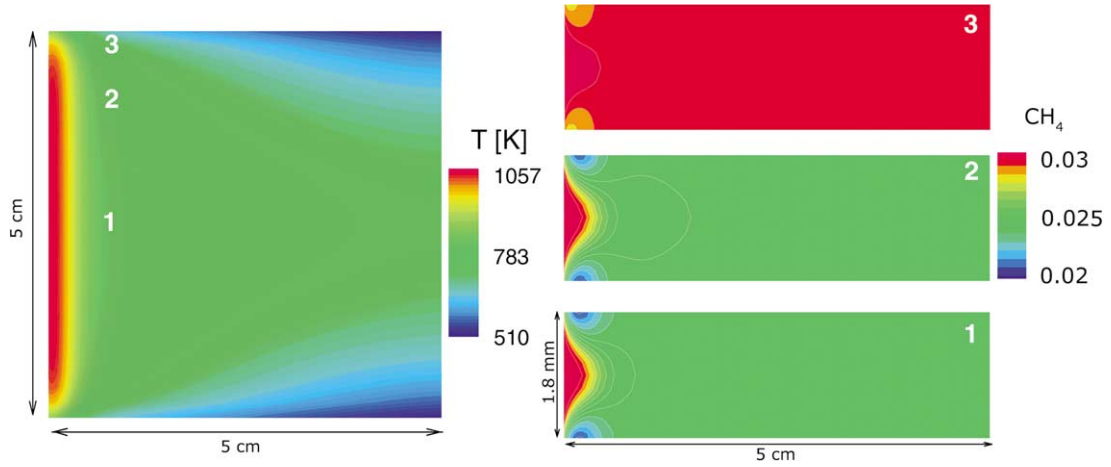

Fig. 3. Temperature profile of the monolith (left) and CH_4 mole fraction profiles for three channels at different positions from transient simulation 15 s after methane feed was increased to 3%. For visibility, the radial coordinate of the channel profiles has been enlarged.

The main objective of this work was to develop a computational tool for the transient simulation of catalytic monoliths using detailed models for chemistry and transport, and thus revealing the transient species and temperature profiles over the monolith. Fig. 3 displays the temperature distribution within the solid bulk and the methane concentration in three selected channels for the above-mentioned transient simulation 15 s after the methane feed has been increased to 3%. Significant features are the hot zone at the inlet, where hydrogen is consumed rapidly, and the slowly decreasing temperature towards the boundary. As the temperature profile for the two inner channels does not vary distinctly, their methane mole fraction profiles look similar. The conversion inside the outer (2) channel has advanced slightly slower than in the central one (1). In contrast, there is hardly any conversion in the channel (3) close to the surface of the monolith.

The application of more complex geometrical structures in three dimensions may result in an even

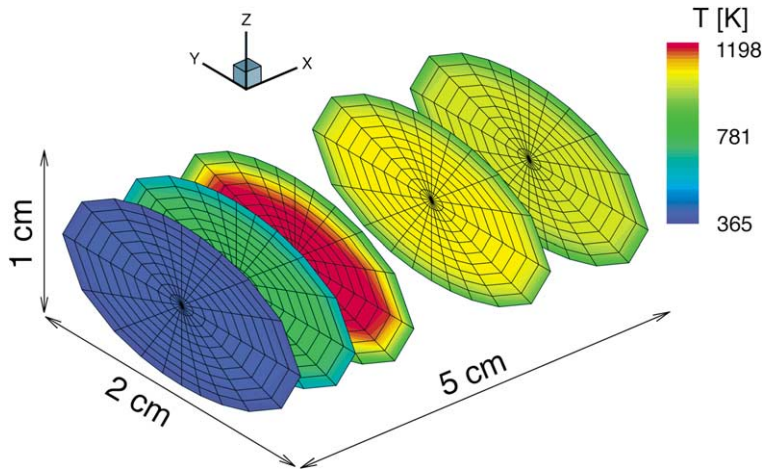

Fig. 4. Three-dimensional temperature profile of a catalyst with elliptical cross-section. The monolith at 1000 K is fed for 5 s with a 3.5 vol.% methane-in-air mixture at 300 K and 0.8 m/s.

larger variety of temperature profiles, which increases the number of channels to be calculated. In Fig. 4, the temperature profile of a catalyst with elliptical cross-section is shown. The calculation started with a monolith at 1000 K. A lean methane/air mixture containing 3.5 vol.% methane at 300 K and a velocity of 0.8 m/s is fed to the monolith. The figure shows the catalysts' temperature after 5 s. The zones in the monolith, where cooling by the fresh gas and heating by combustion occur, become clearly visible. The monolith has not reached steady-state yet.

4. Summary

In this paper, we have presented a new method to capture transient two- or three-dimensional simulations of monolithic catalysts under consideration of detailed models for the chemical reactions and transport processes. The discussed approach of the alternating calculations of the steady-state single-channel flow fields and the transient thermal behavior of the monolith is applicable as long as the residence time of the reactive mixture in the monolith is small compared to the thermal response of the solid bulk and variations in the inlet conditions. This assumption is valid for a wide range of applications such as catalytic combustion and conversion of natural gas and automotive catalytic converters. In these devices, the reactants' residence time is of the order of milliseconds, while the temperature variations of the monolithic structure occur on a time scale of seconds.

As an example, the simulation code was applied to study hydrogen-assisted catalytic combustion of methane in platinum-coated honeycomb monoliths. A boundary-layer formulation of the transport equations was used for single channels, which is a good approximation sufficiently accounting for effects caused by radial diffusion. In combination with detailed models for surface and gas phase reactions, a high resolution of the local processes is achieved.

The transient behavior during the light-off process was described in detail, e.g., while a large amount of methane is converted in the hot inner channels during light-off, almost no methane is consumed in the colder outer channels.

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