

# Transient two-dimensional simulations of monolithic catalysts using detailed models for heterogeneous and homogeneous reactions and transport phenomena for the catalytic partial oxidation of lower alkanes

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## Summary

The application of a newly developed computational tool, DETCHEM<sup>MONOLITH</sup>, for the transient two- and three-dimensional simulations 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 catalytic partial oxidation of methane.

## 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. 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, due to computational complexity, 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 of 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 the present 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<sup>MONOLITH</sup>, 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 catalytic partial oxidation of methane on rhodium-coated foam monoliths, which is a promising alternative to conventional steam reforming for the manufacture of syngas.

## 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.

### Single channel

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 and their stiffness, a numerical solution is computationally expensive [6,8]. Therefore, simpler models such as plug-flow or boundary-layer models [9,10] are frequently used.

In the boundary layer of a fluid near a 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. 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 [11]. The transport coefficients for radial diffusion and the species diffusion flux depend on temperature and species composition. Surface and gas phase reaction source terms are modeled by elementary-step based reaction mechanisms using the DETCHEM computer package [12]. 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 [13] and can be included when necessary.

### Monolithic catalyst

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. The material properties (density, heat capacity and thermal conductivity) 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 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.

## Application

Catalytic partial oxidation (CPO) of methane to syngas in short-contact-time reactors is an interesting alternative to steam reforming. The advantages of this process are the high syngas selectivities and yields (both above 90 % on rhodium-coated monoliths), high throughput due to short contact time, compact reactor shape, low demand of catalyst material and mild exothermicity [14,15]. However there are some disadvantages mainly connected to the high reactor temperature above 1100 K: the reactive mixture may undergo homogeneous gas-phase reactions leading to flames and explosions, and local hot spots due to total oxidation can cause material problems such as

thermal stresses in the support and decrease in catalytic activity due to catalyst sintering and loss. Hence, the numerical simulation of such a process is important to understand the physical and chemical processes occurring.

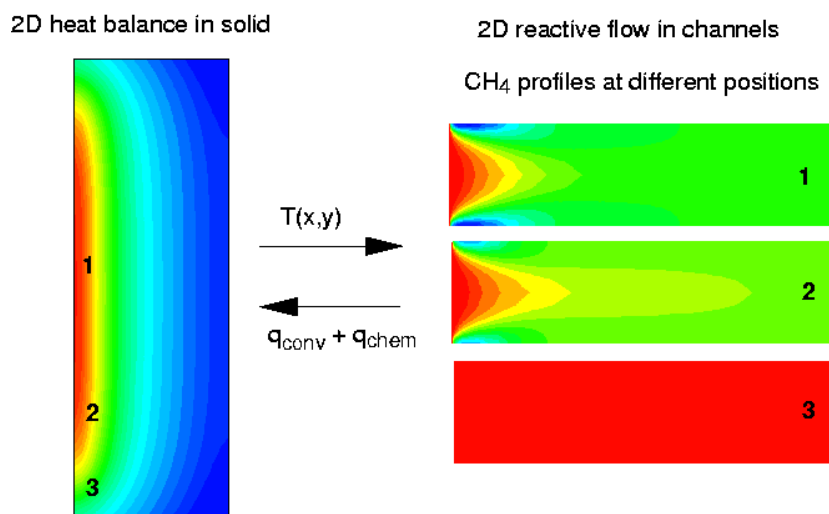
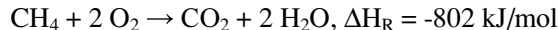
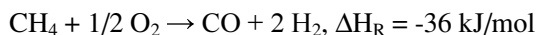


Figure 1: Predicted temperature distribution in the solid structure of the monolith (left) and methane mass fraction in three monolith channels (right) during light-off of CPO of methane over Rh coated extruded monolith.

Detailed chemical mechanisms based on elementary reactions describing the surface kinetics have been developed and have been used to simulate a single channel of this process using the commercial CFD code FLUENT which was coupled with external subroutines to describe the chemistry [6,12]. Globally, the formation of syngas from methane / oxygen mixtures on noble metal catalysts is characterized by the competition between a complete oxidation reaction written as



and a partial oxidation reaction path written as



The influence of gas-phase chemistry on the overall conversion can be neglected at atmospheric pressure [6], hence the simulations were carried out only with surface chemistry. The chemical reactions on the surface were modeled using 38 elementary reactions among 6 gas-phase species and 11 surface species. However, gas-phase chemistry can be used when required, for e.g. at higher pressures.

Light-off of an initially cold catalytic monolith by preheating the incoming feed is discussed as an example. The cylindrically shaped monolith, 1 cm in length and 2.3 cm in diameter, has a channel density of  $62 \text{ cm}^{-2}$  with a single channel diameter of 1 mm. The inner walls are coated with rhodium catalyst. Heat losses at the front and back sides of the monolith, where heat shields prevent severe heat loss, are neglected. An external heat transfer coefficient of  $45 \text{ W/m}^2\text{K}$  and an emissivity of 0.3 are applied at the outer surface of the monolith. The material properties of cordierite are used for the estimation of the radial and axial density, heat capacity and thermal conductivity of the monolithic structure. The parameters correspond to experiments currently carried out in our group.

A methane / oxygen mixture (volume ratio 2:1, 20%  $\text{N}_2$  dilution) preheated to 800 K flows at atmospheric pressure in the catalytic channels with a uniform inlet velocity of 1 m/s. The inlet conditions are kept constant in time and radial distribution. The hot gas stream slowly heats up the solid structure. The onset of the exothermic partial oxidation reaction further increases the monolith temperature.

Figure 1 reveals the temperature distribution in the solid structure and the methane mass fraction in three representative monolith channels after 19 seconds of operation. The front side of the monolith is already heated up. Due to external heat losses at the outer boundary, the temperature there is much smaller than in the center of the

monolith. In that central zone, significant methane conversion occurs as shown in the plots of channels 1 and 2. In contrast to that, no conversion occurs in channel 3 which is closer to the monolith boundary.

## Conclusions

In this paper, a new method was presented 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 behaviour of the monolith is applicable as long as the residence time of the reactive mixture in the monolith is small compared to 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, 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 the partial oxidation of methane. 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 reactions a high resolution of the local processes is achieved. The transient behavior of the monolith was described in detail, e.g., while a large amount of methane is converted in the hot inner channels, almost no methane is consumed in the colder outer channels.

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