

Towards a better understanding of transient processes in catalytic oxidation reactors

Renate Schwiedernoch^a, Steffen Tischer^a, Hans-Robert Volpp^b,
Olaf Deutschmann^a

^aInstitute for Chemical Technology, University of Karlsruhe, Engesserstr. 20,
76313 Karlsruhe, Germany, deutschmann@ict.uni-karlsruhe.de

^bInstitute of Physical Chemistry, Heidelberg University, INF 253, 69120
Heidelberg, Germany

ABSTRACT

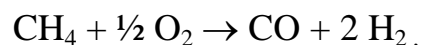
Light-off of the partial oxidation of methane to synthesis gas on a rhodium-coated cordierite honeycomb monolith at short contact times is studied experimentally and numerically. The objective of this investigation is a better understanding of transient processes in catalytic oxidation reactors. The numerical simulation predicts the time-dependent solid-temperature distribution of the entire reactor and the two-dimensional flow fields, species concentrations, and gas-phase temperature profiles in the single channels. A detailed reaction mechanism is applied, and the surface coverage with adsorbed species is calculated as function of the position in the monolith. During light-off, complete oxidation of methane to water and carbon dioxide occurs initially. Then, synthesis gas selectivity slowly increases with rising temperature. The numerically predicted exit temperature, conversion, and selectivity agree well with the experimentally derived data.

1. INTRODUCTION

Several promising production routes in the area of natural gas conversion are based on high-temperature (approximately 1000°C) catalysis at short contact times [1-3]. These processes are often carried out in monolithic structures coated with the catalytic material, in which the explosive gas/oxygen mixture is fed. The understanding of the reactor behavior at transient conditions is crucial for the overall performance, scale-up, and, in particular for reactor safety. Reliable models and computational tools can help in the identification of parameter regions (temperature, mixture composition, pressure, reactor geometry), at

which unsafe reactor operation occurs and assist in the development of a safe reactor design and operation.

In this paper, we apply a new approach for modeling the transient states of catalytic monoliths such as light-off and shut-down of the reactor as well as oscillating behavior and temporal as spatial variations of the feed. Exemplarily, we will discuss the light-off of the catalytic partial oxidation (CPO) of methane to synthesis gas,



over a rhodium coated cordierite honeycomb monolith at short contact times. In the experiment, exit gas-phase temperatures and species concentrations are monitored by thermocouples and mass spectroscopy, respectively. In the numerical study, the recently developed computational tool DETCHEM^{MONOLITH} [4-6] is applied, which permits the three-dimensional simulation of the temperature distribution of the entire monolith coupled with two-dimensional laminar reactive flow field simulations of a representative number of single monolith channels. The latter predicts the gaseous velocity, species concentrations, temperature profiles, and surface coverage based on a multi-step heterogeneous reaction mechanism.

2. EXPERIMENT

The reactor set-up is described in our recent study on CPO of methane on a rhodium/alumina monolith [5]. In contrast to this work, we now use cordierite as support material. The reactor consists of a 40 cm long quartz tube with a diameter of 8 mm. The Rh coated honeycomb monolith, placed inside the tube, is of 10 mm length and 6 mm in diameter. The hydraulic diameter of the single channels, which have a rectangular cross-section, is 0.7 mm. A 10 mm long inert monolith in front of the catalyst serves as radiation shield. A ceramic cloth is wound around both monoliths preventing gas bypass.

The exit gas phase temperature is monitored using a type N thermocouple, which is placed in a quartz nose behind the monolith. The product composition is determined by mass spectroscopy (QMS) as function of time.

In the example discussed, a constant molar inlet CH_4/O_2 ratio of 1.6 with 78 vol.%, Ar dilution is chosen. The mixture flows at 298 K and atmospheric pressure with a total mass flow of 1.7 slpm into the quartz tube reactor. This flow rate corresponds to a single channel inlet velocity of 2.0 m/s and a residence time of few milliseconds.

A furnace is applied to ignite the reaction by heating up the monolith using a temperature ramp of 5 K per minute. As soon as light off occurs, the furnace was turned off. Here, light-off is defined as the rapid increase of conversion

detected by the QMS, which occurs at 850 K for the conditions chosen.

3. MODELING

The model couples the heterogeneous reactions on the catalytic surface, the reactive flow field in the single channels, and the heat balance of the solid structure of the monolith as well as the thermal insulation, quartz tube and monolithic heat shield in front of the reactor. The laminar reactive flow in the single channels is modeled by the steady-state, two-dimensional (axi-symmetric) boundary layer equations with transport coefficients that depend on composition and temperature [7]. Surface and gas phase reactions are modeled by elementary-step like reaction mechanisms. The catalytic reaction on the wall takes a varying surface coverage of adsorbed species along the channel wall into account.

The residence time of the reactants inside the single channel is much smaller than the time scale for temperature variation in the monolith solid due to the larger heat capacity of the solid monolith compared to that of the gas flow. Therefore, the simulation of the flow through a single channel can be treated as steady-state at during one time step of the transient simulation of the heat balance of the solid structure. The heat flux from the gas phase into the monolith bulk, due to convection and chemical reactions, is then calculated for the solid temperature profiles and initial flow conditions by simulation of a representative number of single channels at each time step. Hence, a transient heat conduction equation is solved leading to time-varying temperature profiles for the single channel simulations as well. Heat losses due to radiation and convection at the exterior boundary/insulation of the monolith are taken into account. Based on these models, the recently developed computational tool DETCHEM^{MONOLITH} predicts the two/three-dimensional temperature profiles, species concentrations, and velocity distribution of the entire structured catalyst as function of time. For a more detailed description of the model and the software it is referred to [4-6].

A detailed surface reaction mechanism is applied to model the partial and complete oxidation of methane on rhodium. Since this mechanism also takes intermediate steps and species into account, further global reactions such as steam and CO₂ reforming and the water gas shift reactions are automatically included. The detailed surface reaction mechanism was taken from our former study [5] and consists of 38 reactions among 6 gas phase species and 11 surface species. The simulation also includes a very detailed gas-phase reaction mechanism of up to 414 reactions among 35 species. However, gas phase reactions are not significant at the conditions chosen and will, therefore, not be discussed further in the current paper.

In order to describe the catalyst loading, the ratio of active catalytic to geometrical surface area has to be specified, which can be derived from

Table 1

Properties of the solid and insulation material [8]

physical properties	cordierite monolith	insulation
heat conduction λ_{rad} [W/(m K)]	2	1.36
density ρ [kg/m ³]	2100	2205
heat capacity c_p [J/(kg K)]	800	730

chemisorption measurements. The surface reaction mechanism applied was derived for a Rh/alumina catalyst [5] and it was found that the now used catalyst based on cordierite has only a tens of the active catalytic surface area.

The material properties of the support and the insulation are given in Table 1. The total porosity of the monolithic structure is 0.495. Heat losses due to conduction, convection, and thermal radiation at the exterior walls of the monolith are included in the simulation.

4. RESULTS AND DISCUSSION

Figure 1 (left) shows the numerically predicted temperature distribution of the solid structure during light-off. The time is set to zero when the conversion of methane rapidly increases. At this time the furnace, which was used to heat up both the inert and the catalytic monolith, is switched off. The cold inflowing gas is heated up (Fig. 1 middle) and an almost homogeneous temperature distribution occurs.

It can clearly be seen how the reaction starts at the front end, there methane is oxidized, mainly to CO₂ and H₂O (Fig. 2), and the temperature increases. Further downstream, only little conversion occurs. During ignition radial temperature profiles are established over the entire monolith due to external heat losses (the furnace is turned off now) as well as in the single channel, where the exothermic heterogeneous reactions lead to higher temperatures on the catalytic wall. After approximately 2s, a hot spot occurs in the first section of the catalytic monolith. After 50 s, the solid temperature profile is smoothed out due to heat conduction the solid structure and the steady state is reached.

In our former study [5], in which an alumina support was used, the reaction started at the back end of the monolith and no hot spot was observed. It should be noted that not only the different heat conduction of the support matters but also the total catalyst loading, monolith porosity and geometry. The detailed simulation offers a useful tool to study the impact of these different external parameters on reactor performance, in particular at transient conditions.

The product profiles in the single channel (Fig. 2) reveal that total oxidation is the main reaction during light-off leading to a the fast temperature increase. The only slightly exothermic formation of synthesis gas begins slowly with increasing temperatures. It can also be seen that a large part of the formed hydrogen comes from a consecutive reaction, in which the steam, mainly formed

in the entrance region of the catalyst where a large amount of oxygen is still available, reacts with methane. This endothermic reaction causes the slight temperature decrease further downstream aside from heat losses.

The much faster diffusion of hydrogen in comparison to the other species leads to the different shape of the radial profiles, which also means that the processes in the single channel need to be modeled by a two-dimensional description as done here; the overall reaction is transport-limited after ignition.

It is also worth to mention that the overall conversion reaches a maximum a few seconds after ignition, which seems to be caused by the interaction of different heat transport modes. Thus, the ambient temperature, which is still close to the initial furnace temperature, the initially very high total oxidation rate releasing a large amount of reaction heat and leading to the temperature peak discussed, and the still relatively warm heat shield have a large impact on the chemical processes during light-off.

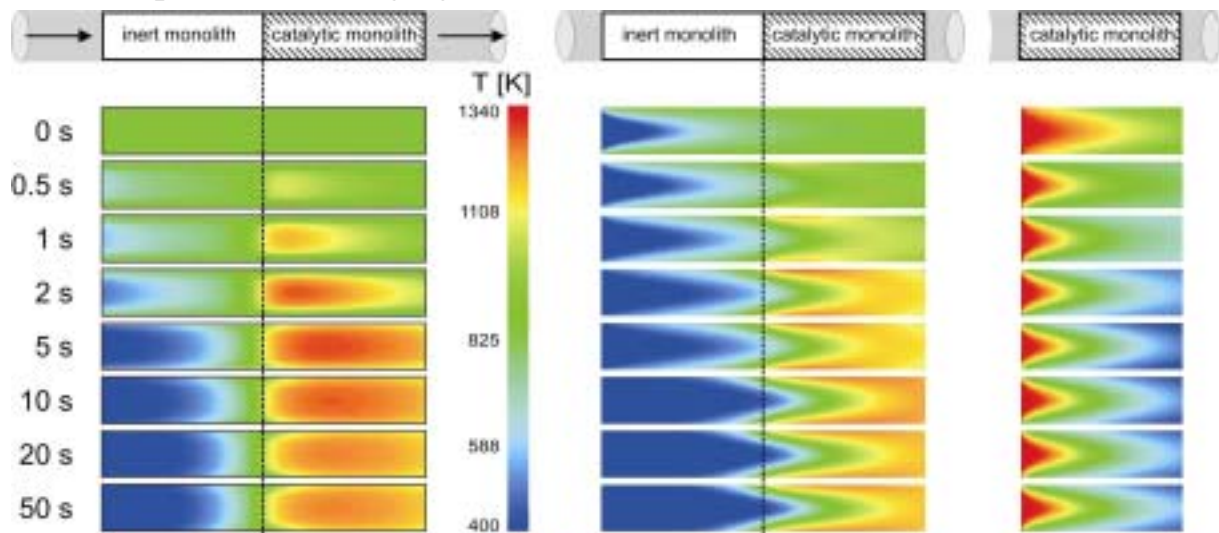


Fig. 1. Temperature of the solid structure of the monoliths (left), gas-phase temperature (middle) and methane mole fraction (right, range: 0.0-0.137) in a single channel in the center of the monolith during light-off; the radial coordinates are stretched differently.

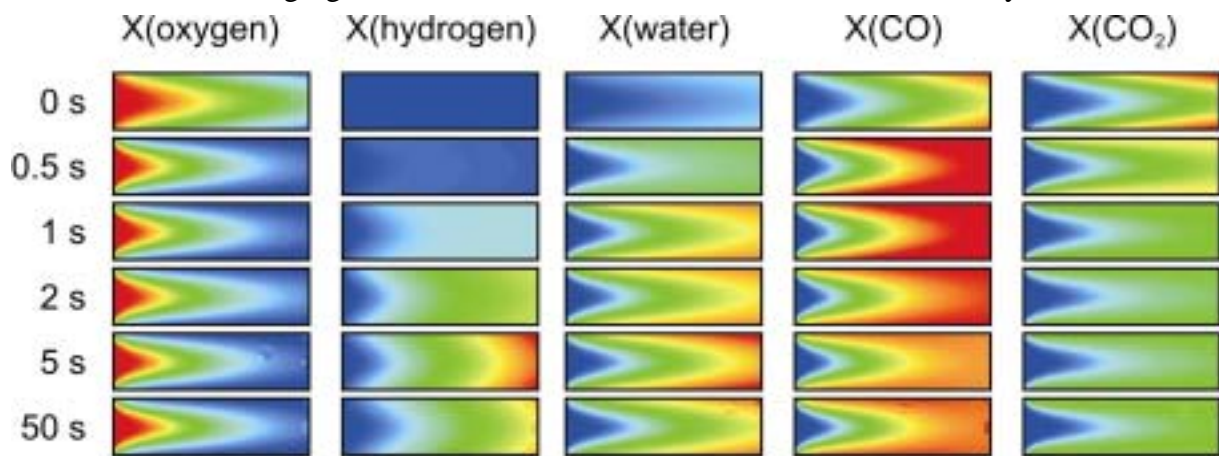


Fig. 2. Gas-phase mole fractions in a single channel in the centre of the monolith during light-off; the radial coordinates is stretched. (ranges: O₂ = 0 - 0.08, H₂ = 0 - 0.05, H₂O = 0 - 0.07, CO = 0 - 0.05, CO₂ = 0 - 0.03)

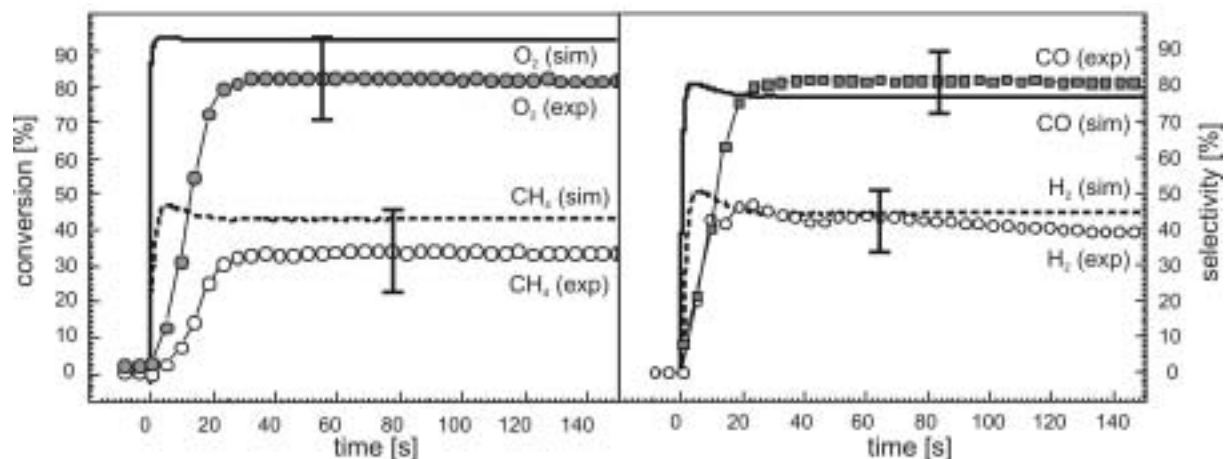


Fig. 3. Comparison of experimentally derived and numerically predicted conversion and selectivity.

A qualitatively good but not perfect agreement between experimentally derived and numerically predicted conversion and selectivity as function of time could be achieved.

The model and computer code applied offers a useful tool to reach a better understanding of transient processes of catalytic oxidation reactors. They can now be applied to explore safe parameter regions for reactor design and operation.

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