Experimental and Numerical Studies of the Transient Behavior of Catalytic Monoliths

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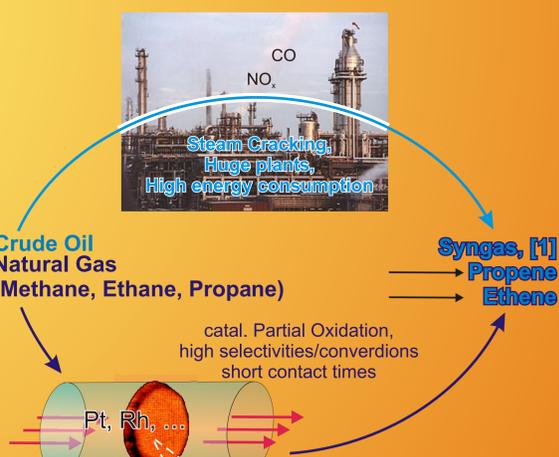**Interdisciplinary Center for Scientific Computing (IWR), Universiy of Heidelberg**

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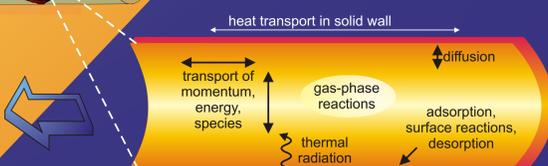
Motivation

⇨ The Catalytic Partial Oxidation (CPO) of methane on Rh coated monoliths in short contact time reactors is a promising route to convert natural gas to syngas and finally higher hydrocarbons.[1]

⇨ Such commercial applications of high-temperature catalysis depend on controlling the operation of the reactor at transient conditions such as light-off, extinction of reactions, homogeneous ignition, and aging of the catalysts. These problems call not only for transient experiments but also for transient numerical simulations.

⇨ While previous work focused on steady-state conditions,[2] we develop now detailed Mmodeles for transient behavior of "short-contact-time" reactors.

CO
NO$_x$

Steam Cracking
Huge plants
High energy consumption

Crude Oil
Natural Gas
(Methane, Ethane, Propane)

Syngas, [1]
Propene
Ethene

catal. Partial Oxidation, high selectivities/converdions short contact times

Pt, Rh, ...

The 2D and 3D Navier-Stokes equations are solved, which are coupled with detailed transport and chemistry models. Furthermore we need to consider to couple the reactive flow in the single channels with the overall heat transport in the solid structure

heat transport in solid wall

diffusion

transport of momentum, energy, species

gas-phase reactions

adsorption, surface reactions, desorption
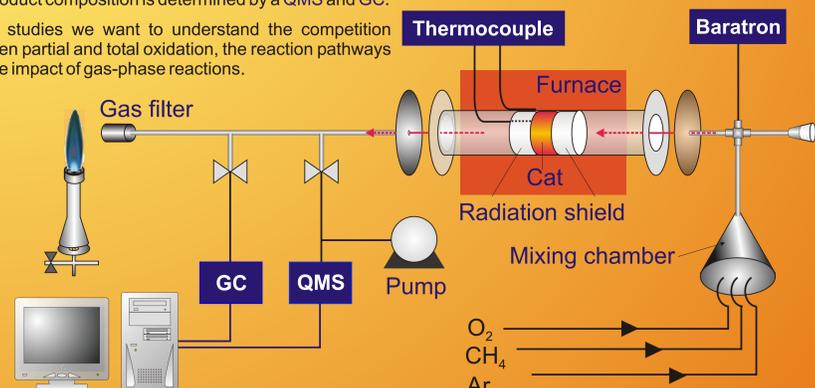
thermal radiation

Experimental Setup

⇨ The reactor consists of a 25 cm long quartz tube. An alumina monolith, coated with 3 wt-% Rh, 6 mm in diameter, 5 mm length, and 24 channels is placed inside.

⇨ The reaction is ignited by heating up the monolith with a furnace and can be run autothermally (~ 1200 K) or temperature controlled.

⇨ The gases are fed into the reactor at following conditions: u_0 = 1.0 m/s (GHSV = 1.96·10^6 h^{-1}), T_0 = 300 K, T_{ign} = 690 K, p_{CH4}/p_{O2} = 1.7, 80% Ar dilution, P_{tot} = 1.1 bar. This results in a residence time of some milliseconds .
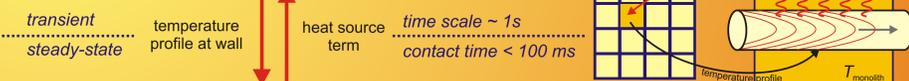
⇨ The product composition is determined by a QMS and GC.

⇨ In our studies we want to understand the competition between partial and total oxidation, the reaction pathways and the impact of gas-phase reactions.
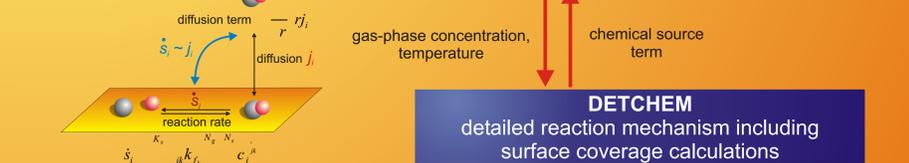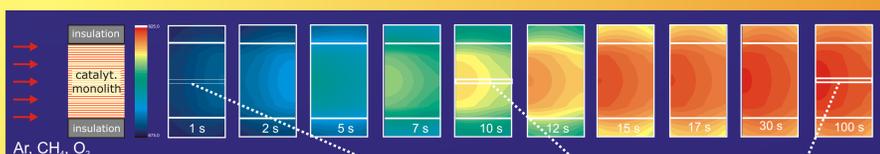
Thermocouple
Baratron
Furnace
Cat
Gas filter
Radiation shield
Mixing chamber
GC
QMS
Pump
O$_2$
CH$_4$
Ar

DETCHEM^{MONOLITH}, [3]

MONOLITH
temperature of the solid structure by a 2D / 3D - heat balance

transient / steady-state

temperature profile at wall

heat source term

time scale ~ 1s
contact time < 100 ms

MONOLITH
channel density
heat source term
T_{gas}
temperature profile
$T_{monolith}$

CHANNEL
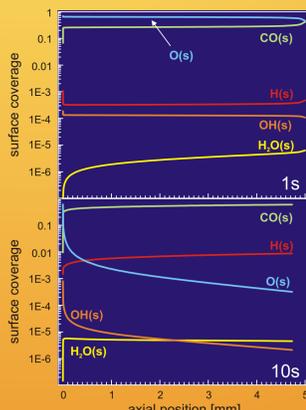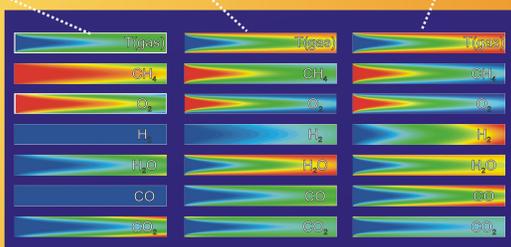simulation of the 2D flow field by a boundary layer approach in a representative number of monolith channels

diffusion term $\quad -\ rj_i$

diffusion j_i

gas-phase concentration, temperature

chemical source term

reaction rate

DETCHEM
detailed reaction mechanism including surface coverage calculations

Temperature, Selectivities, Conversions

Comparison between simulation and experimental derived data

T [K]
T(adiabatic)
Experiment (exit, gas phase)
Simulation (exit, gas phase)
690 K

selectivity [%]
CO
H$_2$

conversion [%]
O$_2$
CH$_4$

time [s]

Time dependent change of temperature, syngas selectivity, and conversions in a Rh/Al$_2$O$_3$-monolith

⇨ The Simulation is based on a recently developed surface reaction mechanism on Rhodium.[4]

⇨ Symbols = experimental data
Lines = simulation

⇨ The numerically predicted exit gas-phase temperature, H$_2$ and CO selectivities, and oxygen and methane conversion, agree well with the experimental data.

⇨ At the ignition point only little CO and no H$_2$ are produced. Then syngas selectivity increases rapidly.

⇨ Oxygen breakthrough is caused by relatively large channel diameter of 0.74 mm compared to the 5 mm catalyst length.

⇨ No impact of gas-phase reactions were observed at those conditions, however, they become significant at elevated pressure.

⇨ The experiment and, in particular, the computational tools will be used to study more complex chemical systems and support reactor design and scale-up

Simulated Temperature and Species Profiles during Ignition

insulation
catalyt. monolith
insulation

Ar, CH$_4$, O$_2$

1 s | 2 s | 5 s | 7 s | 10 s | 12 s | 15 s | 17 s | 30 s | 100 s

⇨ The incoming cold gas is heated up by the preheated monolith. First reactions start at the back end of the catalyst.

⇨ The total oxidation of CH$_4$ to CO$_2$ and H$_2$O heats up the monolith temperature. The reaction zone moves to the front end of the catalyst. No CO and H$_2$ is formed at the beginning.

⇨ With increasing temperature O$_2$ is rapidly consumed, and CO is formed at the channel exit. At 10 s first H$_2$ formation occurs by steam reforming. With higher temperatures H$_2$ and CO formation increases while CO$_2$ and H$_2$O decrease.

surface coverage

CO(s)
O(s)
H(s)
OH(s)
H$_2$O(s)
1 s

CO(s)
H(s)
O(s)
OH(s)
H$_2$O(s)
10 s

axial position [mm]

⇨ The surface is mainly covered by oxygen before ignition, which leads to a low reaction rate and

⇨ the system is controlled by surface reaction kinetics

⇨ The high oxygen sticking leads to Rh-oxide which increases the total amount of oxygen available for later reactions on the surface.
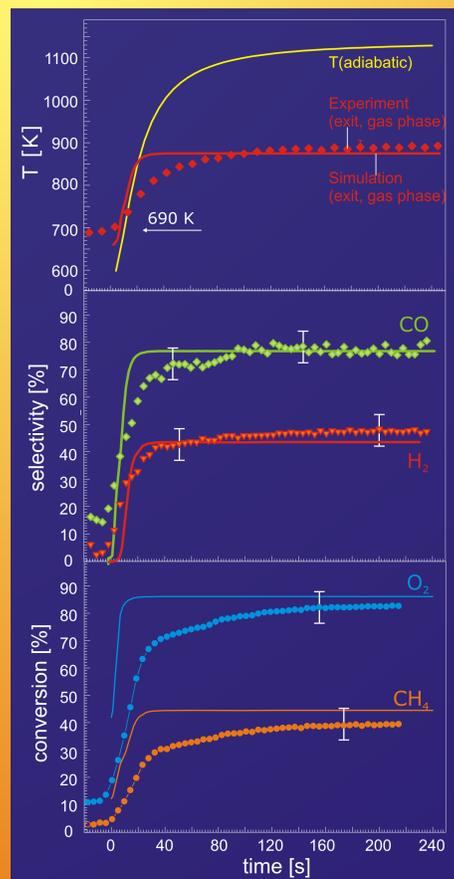
⇨ With Increasing temperature the adsorption desorption-equilibrium for oxygen shifts slowly towards desorption resulting in more and more vacancies on the surface. Ignition occurs.

⇨ After ignition, the overall reaction is controlled by radial heat and mass transport.

⇨ Significant oxygen coverage can only be seen at the catalyst entrance where complete oxidation of methane occurs.

References:

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[3] O. Deutschmann, C. Correa, S. Tischer, D. Chatterjee, J. Warnatz, DETCHEM-PACKAGE (Version 1.5.3)
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