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Experimental and numerical investigation of the catalytic partial oxidation of methane on rhodium coated honeycomb catalysts

Summary

The catalytic partial oxidation (CPO) of light alkanes on the noble metals Pt and Rh at very short contact times has been shown to offer a promising route to convert natural gas into more useful chemicals such as synthesis gas, higher hydrocarbons, and oxygenates.[1,2]

The catalytic reactor used for these process, such as foam or extruded monoliths, wire gauzes, or sintered spheres, show a complex interaction of transport and chemical reactions occuring on the catalytic surface and in the gas phase. Therefore, the description of the reactor requires detailed models of the flow field, chemistry and their coupling.

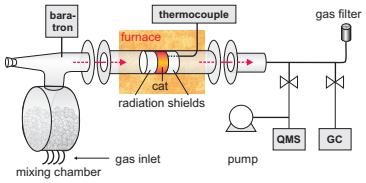
We studied the chemical reactions at the Rh and Pt surfaces for the partial oxidation of methane, and the coupling with the surrounding reactive fluid flow.

Selectivitiy, conversion, and reactor temperature as function of temperature, velocity, and methane/oxygen-ratio derived from a detailed numerical simulation are compared with experimental data.

The simulation applies elementary step reaction mechanisms for gas phase as well as surface chemistry, which are coupled with three- and two-dimensional flow field simulations including detailled models for mass and heat transport. The computations are based on the CFD-code FLUENT which is coupled with the chemistry modeling package DETCHEM.[3]

The study reveals that partial oxidation of methane is a purely heterogeneous process at atmospheric pressure, while homogeneous (gas phase) reactions become significant at elevated pressure.[4]

Experiment



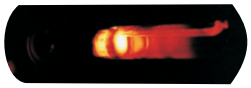
The experimental setup was designed in a way that permits the application of detailed models for all processes occurring in the reactor.

The reactor consists of a quartz tube with various diameters (2.5 cm, 1.5 cm, and 0.8 cm) containing a 1 cm long honeycomb monolith with a well defined rectangular shape of its channels. The monoliths are coated with the noble metals Pt or Rh.

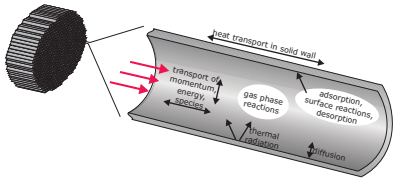
The entire reactor can be run either autothermally or temperature controlled by a furnace. Temperatures are monitored using thermocouples inside and at the exterior wall of the reactor.

The product composition is determined by mass spectroscopy and gas chromatography.

The reactor is operated at atmospheric pressure. The total feed flow rate corresponds to a residence time of few milliseconds.



Physical and chemical processes in a monolith channel



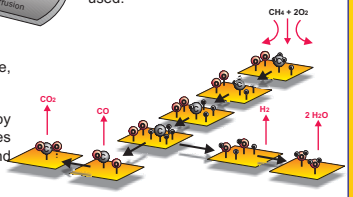
The surface reaction mechanism for modeling the oxidation of methane and ethane on rhodium and platinum consists of up to 82 reactions.[5]

Additionally up to 414 gas phase reactions among 35 species are used.

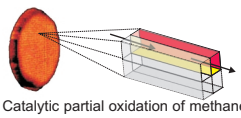
Because all channels behave essentially alike, only one channel needs to be analyzed.

The single channel of the monolith is modeled by the two- and three-dimensional Navier-Stokes equations with transport coefficients that depend on temperature and composition.

Heat transport in the channel wall is taken into account.



CPO of methane to syngas at 1 bar: 3D - simulation



Catalytic partial oxidation of methane on a rhodium coated extruded monolith.

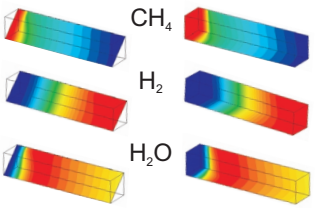
$CH_4 + 1/2\ O_2 \rightarrow CO + 2\ H_2$

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

Initial conditions: T_u = 855 K, u_s = 0.67 m/s, T_{wall} = 855K, P_{tot}/P_{O2} = 1.8 (90% N_2), 11 x 0.5 x 0.5 mm

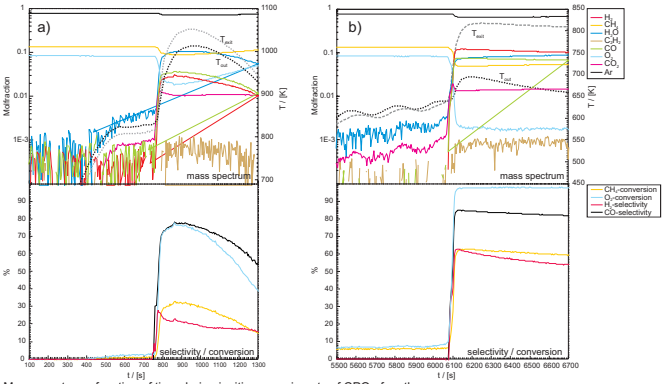
Species mass fraction

diagonal face inlet, wall, symmetry face



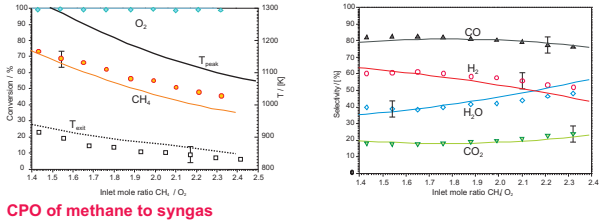
Catalytic CH_4 conversion starts at the channel inlet where partial and complete oxidation occur. Steam reforming occurs farther downstream where O_2 is alredy completely consumed.

Ignition experiments with different supports



Mass spectra as function of time during ignition experiments of CPO of methane.
CH_4/O_2-ratio = 1.6, 75% Ar, P = 800 torr, velocity = 1 m/s, monolith diameter = 6 mm, length = 10 mm; rhodium coated monoliths made out of cordierit (a) and aluminia (b); the exit temperature was measured directly behind the catalyst and the outside temperature at exterior wall of the quartz tube.

Comparison of experiment and numerical simulation



CPO of methane to syngas

Effect of inlet mole methane / oxygen ratio on selectivity, conversion, peak an outlet temperature, symbols = experiment, lines = simulation.

Conclusion

- Experimentally derived and numerically predicted conversion and selectivity of the CPO of methane agree very well.
- 3D-Simulations of a single channel of the monolith reveal the importance of steam reforming.
- Understanding of ignition is crucial for reactor safety. Experiments show that aluminia monoliths - compared to cordierit - are more stable and lead to higher syngas selectivity and methane conversion.
- Future work will include transient simulations.

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