

DETAILED MODELLING OF SHORT-CONTACT-TIME REACTORS

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Abstract: Light alkanes can be converted to more useful chemicals in noble metal coated monoliths at very short contact times. The short-contact-time reactor is described by detailed models for the flow field, chemistry, and their coupling. The partial oxidation of methane to synthesis gas in a rhodium coated monolith is studied numerically as an example.

Keyword: reactor modelling, catalytic partial oxidation, natural gas, CFD, kinetics

INTRODUCTION

Light alkanes can be converted to more useful chemicals such as syngas (H_2 and CO), higher hydrocarbons, olefines, and oxygenates on noble metal coated monoliths at very short contact times [1-5]. The industrial application of these partial oxidation processes is expected to have a significant impact on the utilisation of natural gas as chemical feedstock. The catalytic reactors are based on foam or extruded monoliths, wire gauzes, or sintered spheres, coated with noble metals such as platinum and rhodium. The reactor is also called short-contact-time reactor due to the short residence time of approximately one millisecond. The short contact time guarantees a very high throughput using a small amount of catalyst and low energy and capital costs. Some complete combustion of the alkanes to CO_2 and H_2O occurs besides the formation of desired products. These highly exothermic combustion reactions provide the heat to operate the reactor auto-thermally at over 1000 K. Apart from this heat release effect, CO_2 and H_2O however are waste products of the process.

In the present work, the partial oxidation of methane, the main component of natural gas, to syngas in a rhodium coated monolith is studied as an example of short-contact-time reactor modelling. We use detailed models for the transport and both the gas phase and surface reactions. The competition between partial oxidation, forming the desired products H_2 and CO , and complete oxidation, forming CO_2 and H_2O , are discussed. In extension of a former study [6] the adsorption of H , O , and OH radicals on the catalyst is taken into account in the present work.

The industrial application needs the reactor to operate at elevated pressure, but high pressure experiments in conventional laboratories are expensive and dangerous, because the very reactive mixture may explode. However, the developed models and computational tools can rather easily be applied to studying the reactor behaviour at elevated pressure. Hence, detailed modelling and simulation will not only help to understand the complex interactions between reactive flow and catalytic surface but also be used to explore reactor conditions which are beyond available experimental facilities.

NUMERICAL MODEL

The numerical simulation is based on the CFD code FLUENT [7]. The code is well established and can easily be used to set up fluid flow problems and to solve them. However, modelling of detailed chemistry in current versions is limited because of a maximum number of reactions and difficulties to handle stiff chemistry. Furthermore, FLUENT's surface reaction model does not take the surface coverage into account. Therefore, we coupled the FLUENT code to external subroutines that model detailed gas phase and surface chemistry [6]. In this model, the state of the catalytic surface is described by its temperature and the coverages of adsorbed species. The surface coverages vary in the flow direction.

Sketches of laboratory-scale short-contact-time reactor and tubular reactor model are shown in Fig. 1. This tubular reactor serves as a model for a single pore of the monolithic catalyst. Typical pore diameter varies between 0.25 and 1 mm, while the

length of the catalytic part of the reactor is typically 1 cm. In these small diameter channels the flow field is always laminar.

Experimental measurements indicate only small temperature gradients over the catalyst for situations studied in this work. In the simulation, the catalytic wall is assumed to have a constant temperature. An adiabatic, chemically inert wall, 1 cm in length, is used in the model to simulate the experimentally used heat shields in front of and behind the catalytic section.

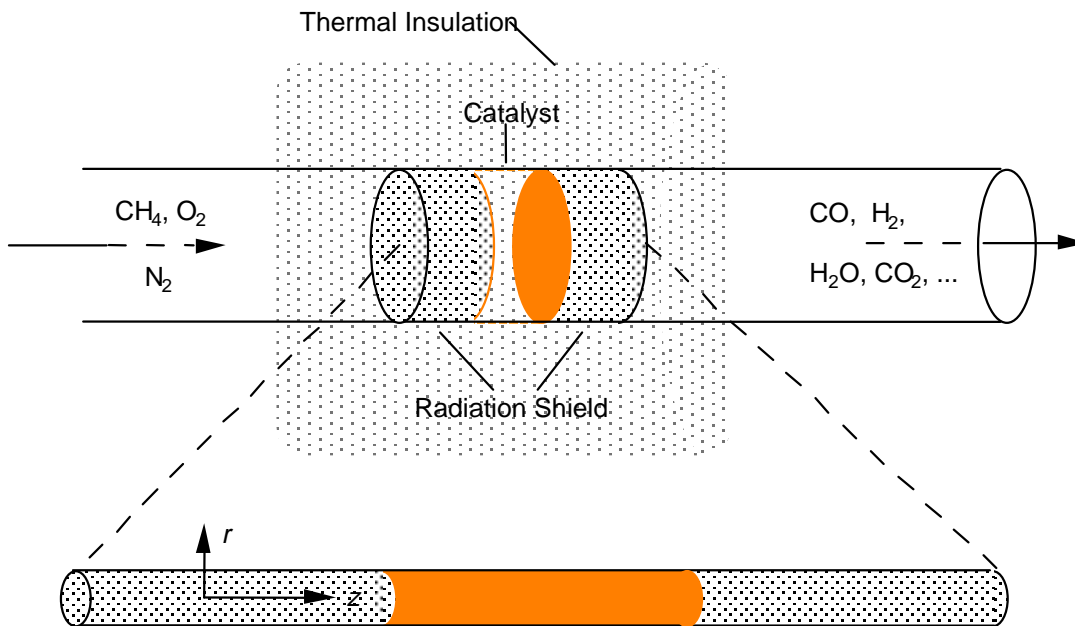
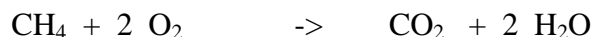


Figure 1: Sketches of a laboratory-scale reactor (top) and the tubular reactor model representing a single pore of the monolith (bottom).

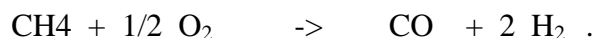
The tube wall catalytic reactor is described by the two-dimensional conservation equations using cylindrical geometry where the axial direction, z , and the radial direction, r , are the independent variables. At the tube centreline, a symmetry boundary condition is applied at which all variables have a zero normal gradient, except the velocity component normal to the boundary. This normal velocity vanishes at the symmetry boundary. A structured grid is used for the simulation; the grid must be very fine around the catalyst entrance to resolve the flow field. The total number of grid points varied between 10^3 and 10^4 depending on reactor diameter and external conditions such as temperature. The number of computational cells with surface reaction boundaries varied between 30 and 100.

CHEMICAL REACTION SYSTEM

The formation of syngas from methane/oxygen mixtures on noble metal catalysts is characterised by the competition between a complete oxidation channel globally written as



and a partial oxidation channel written as



Appropriate catalytic material and residence time must be chosen to achieve high syngas selectivity. Rhodium coated foam catalysts with a residence time of approximately one millisecond are capable of producing syngas selectivity of over 90% with methane conversion of over 90% [5].

The oxidation of methane can occur both on the surface and in the gas phase. It is generally assumed that the influence of gas phase chemistry on the overall conversion can be neglected at atmospheric pressure because the residence time is on the order of one millisecond, a time that is too short to ignite the mixture homogeneously. Furthermore, the radicals formed in the gas phase may recombine on the surface of the small diameter channel inhibiting a chain branching reaction. However, an increasing role of gas phase chemistry is expected with increasing pressure.

The gas phase reaction scheme is based on an elementary-step mechanism developed for hydrocarbon oxidation [8]. This mechanism is reduced by calculation of a homogeneous reactor under given conditions in order to keep the 2-D simulation tractable. The reduction results in a mechanism containing 164 reactions among 22 chemical species. The kinetic data of the pressure dependent reactions are chosen according to the reactor pressure.

A radical pool must be formed before gas phase conversion is fast enough to compete with catalytic conversion. Because of the fast complete oxidation channels, gas phase reactions are expected to decrease syngas selectivity. Aside from this decrease in reactor performance, gas phase chemistry has the potential of flames and explosions and must be understood from a reactor safety point of view.

The surface chemistry model is based on the reaction mechanism developed by Hickman and Schmidt [1] for high-temperature partial oxidation of methane in a short contact time reactor with a rhodium coated foam monolith. The mechanism assumes dissociative methane and oxygen adsorption, formation of CO, CO₂, H₂, and H₂O via OH, and desorption of products. All reaction steps are reversible except methane adsorption and CO₂ desorption. It is assumed that oxygen is adsorbed non-competitively with other species whereas all other species are adsorbed competitively. More details such as reaction order can be found in the original work [1]. We extended this mechanism by three reactions being the adsorption of H, O, and OH radicals. The sticking coefficients for these steps are assumed to be unity.

RESULTS AND DISCUSSION

The simulation of the following case will be discussed as an example of catalytic syngas formation in a partial oxidation reactor: A methane/oxygen mixture (volumetric ratio 1.8, 30% nitrogen dilution) flows at a uniform inlet velocity of 1 m/s and at 298 K into a cylindrical tube 3 cm in length with a diameter of 0.5 mm as sketched in Fig. 1. The 1 cm long catalytic wall has no temperature gradient in the axial direction. The catalyst is assumed to be a film on the wall. The wall is assumed to be adiabatic and

chemically inert before and after the catalytic section. The conditions are close to experiments carried out by Bodke and Schmidt [5] in which a 65 ppi Rh/ α -Al₂O₃ foam monolith was used as catalyst. An auto-thermal reactor temperature of 1073 K was measured by a Pt/Pt-13%Rh thermocouple with an accuracy of ± 50 K and no axial temperature gradients are reported. The total pressure now is 1.4 bar. Figure 2 shows the calculated mass fractions of the reactants CH₄ and O₂ and the main products CO₂, H₂O, CO, and, H₂ as a function of position in the reactor. The catalytic part of the tubular reactor is between 0 and 10 mm axial position (z) and the radial position (r) is set to zero at the tube axis so that the catalytic wall is at $r = 0.25$ mm. The flow direction is from left to right. Methane oxidation starts directly at the catalyst entrance where large radial and axial gradients are formed. At the catalyst exit, however, there is still some methane left, the methane conversion being 90.1%. In contrast to methane, oxygen is completely (99.96%) consumed in the catalytic reactor.

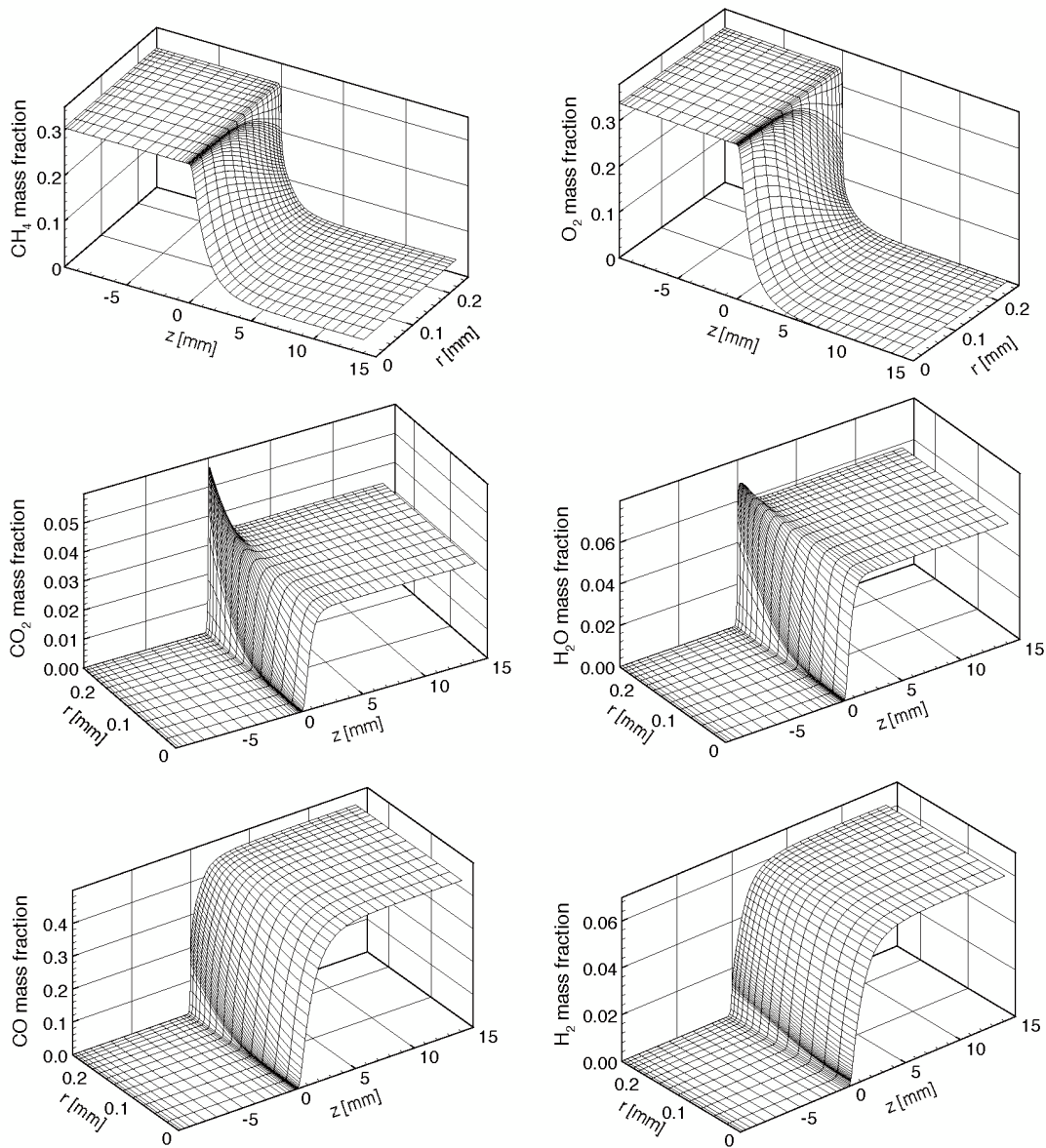


Figure 2: Mass fraction of CH₄, O₂, CO₂, H₂O, CO, and H₂ as a function of position in the reactor at atmospheric pressure.

The formation of hydrogen and carbon monoxide as the desired products and the formation of water and carbon dioxide as the undesired products compete at the catalyst entrance. The strong radial profiles indicate that methane is almost completely oxidised by surface reactions. In the beginning the oxygen concentration is large enough to quickly produce a significant amount of CO_2 and H_2O leading to steep radial concentration gradients of these species. One millimetre downstream from the catalyst entrance, the complete oxidation channels practically extinguishes, although there is still considerable oxygen in the gas phase. In this region oxygen is completely used for CO formation. It should be mentioned that the formation of syngas exceeds the formation of the combustion products even in the first part of the catalytic monolith.

The role of gas phase chemistry in the overall conversion at atmospheric pressure, 1.4 bar, is revealed by a comparison of a simulation with only surface chemistry and a simulation with both surface and gas phase chemistry. Both simulations do not show any significant differences in total conversion and selectivity or in species concentration profiles. The number of radicals such as OH being 10^{10} is too low to initiate gas phase conversion. Hence, gas phase chemistry does not play a significant role for syngas formation on Rh in the reactor at atmospheric pressure.

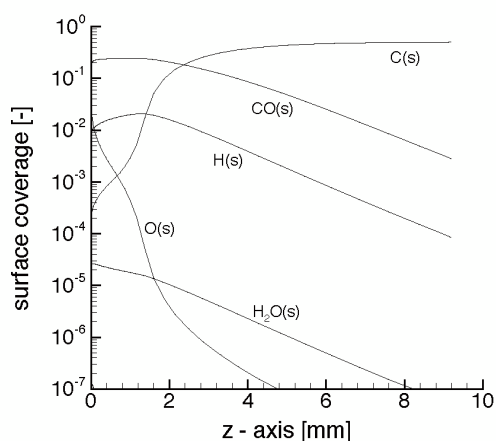


Figure 3: Surface coverage as a function of the axial position (z) in the reactor. The axial position is zero at the catalyst entrance.

The calculation of surface coverage as a function of the axial position in the reactor is shown in Fig. 3. In the catalyst entrance region, the major surface species are $\text{CO}(\text{s})$, $\text{H}(\text{s})$, and $\text{O}(\text{s})$. In this region, the oxygen concentration is still large, explaining the CO_2 and H_2O formation. $\text{CO}(\text{s})$ is formed very fast from $\text{C}(\text{s})$ after dissociative methane adsorption. The rate-limiting step for water production is the $\text{OH}(\text{s})$ formation because $\text{OH}(\text{s})$ immediately leads to water due to the high hydrogen coverage, $\text{H}(\text{s})$. This fast $\text{OH}(\text{s})$ consumption also results in an $\text{OH}(\text{s})$ coverage being lower than 10^{-7} . The activation energy for CO_2 formation is similar to that of OH formation, which results in the production of CO_2 . Farther downstream, the oxygen coverage rapidly decreases, and therefore, any adsorbed oxygen is consumed by formation of $\text{CO}(\text{s})$, which desorbs before it can be completely oxidised.

The straight channel geometry is obviously a simplification of a foam monolith where the pores vary in diameter and length and may be connected. Furthermore, the surface reaction mechanism was established by fitting the experimental results to a one-dimensional model, which neglects transport effects [1]. However, the calculated selectivities (C and H atom based, respectively) and conversion agree quite well with the experimental data: CH₄ conversion is 90.1% (experiment: 88.9%), O₂ conversion 99.96% (100%), H₂ selectivity 90.6% (91.0%), CO selectivity 95.5% (93.5%). The calculated temperature of the catalytic part of the reactor wall is 1070 K, which is determined from conversion and selectivity assuming a global adiabatic process.

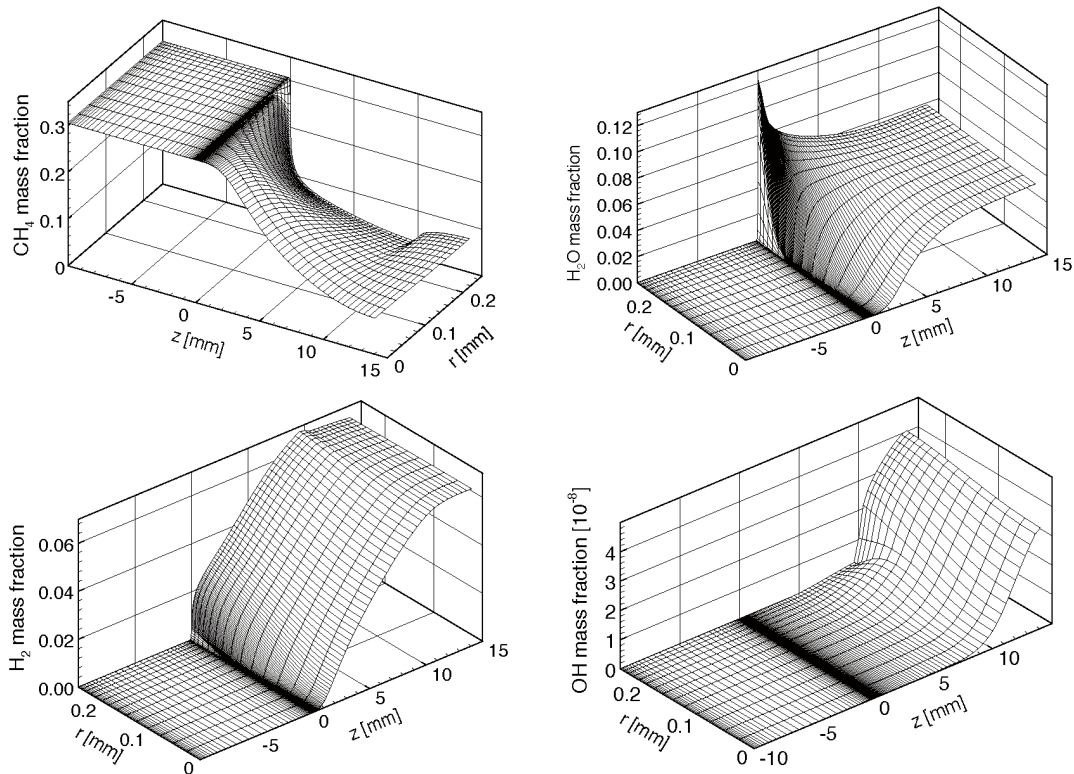


Figure 4: Mass fraction of CH₄, H₂O, H₂, and OH as a function of the position in the reactor at an operating pressure of 10 bar.

The industrial application of short-contact-time reactors depends on the possibility of running the reaction at higher pressures. In laboratory experiments, measurements of the pressure dependence are limited due to safety and costs. Hence, the following simulation explores pressure conditions that are beyond available experimental facilities. Now, the reactor pressure is 10 bar, all other conditions are taken from the atmospheric pressure simulation as discussed above. The temperature of the catalytic wall is kept constant at 1070 K. Figure 4 exhibits gas phase profiles of CH₄, H₂O, H₂, and OH mass fraction, all of them occur in surface and gas phase reactions as well. The reactor is not long enough for complete conversion of methane. In the catalyst entrance region, the complete oxidation takes place on the surface as already shown for atmospheric pressure. However, the formation of the combustion products slowly continues behind this entrance region mainly due to gas phase reactions as shown for H₂O. OH radicals are an important precursor of complete oxidation of

methane. They can not only be formed on the surface and consequently desorb into the gas phase, but also adsorb on the surface and recombine there. Figure 4 reveals that the catalytic surface ($0 \text{ mm} < z < 10 \text{ mm}$) acts as a sink for OH radicals which partly suppressed gas phase reactions. In comparison to the former study [6], where adsorption of O, H, and OH were not taken into account, the present model decreases the influence of gas phase chemistry.

Summarising, gas phase reactions lead to an increase of undesired complete oxidation products at a pressure of 10 bar. A comparison between the full (surface plus gas phase reactions) simulation and one, which neglects gas phase reactions, reveals a decrease of syngas selectivity of only 1% to 3%. However, homogeneous reactions are expected to become more and more significant at even higher pressure of 20 - 30 bar at which an industrial application should be operated. The surface chemistry of radicals, adsorption/recombination versus formation/desorption, plays an important role. Therefore, more reliable kinetics data of radical surface reactions are necessary to quantitatively understand reactor performance at high pressure.

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