Natural Gas Conversion in Monolithic Catalysts: Interaction of Chemical Reactions and Transport Phenomena

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Abstract

The interaction of transport and kinetics in catalytic monoliths used for natural gas conversion is studied experimentally and numerically. The paper focuses on a precise flow field agreement between experiment and model. Therefore, we use extruded monoliths with rectangular channel cross-section and a three-dimensional Navier-Stokes simulation including detailed reaction mechanisms and a heat balance. Latter also accounts for heat conducting channel walls and external heat loss. If a washcoat is used, a set of one-dimensional reaction-diffusion equations is additionally applied for modeling the transport and heterogeneous reactions in the washcoat. Partial oxidation of methane to synthesis gas on rhodium coated monoliths has been studied as example.

1. INTRODUCTION

Monolithic catalysts are often applied for natural gas conversion processes such as partial oxidation of light alkanes [1, 2] and catalytic combustion [3, 4]. In particular at short contact times, a complex interaction of transport and reaction kinetics can occur. Chemical reactions can not only take place on the catalytic surface but also in the gas phase as was shown for partial oxidation of methane on rhodium at elevated pressure [5] and oxy-dehydrogenation of ethane on platinum at atmospheric pressure [6]. In those studies, computational tools for the numerical simulation of heterogeneous reactive flows were developed and applied to a two-dimensional simulation of a single-channel in a foam monolith. In that work, the complex shape of the pores of the foam monolith was described by using the simplified model of a straight tube. A three-dimensional simulation of the catalytic partial oxidation of methane to synthesis gas in a wire gauze configuration has been previously performed by de Smet et al. [7] but a simple surface reaction model was used.

The understanding of the details of the reactor behavior demands a better agreement between experimental and modeled flow field without neglecting the complex chemistry. Therefore, our present work focuses on setting up an adequate experiment where we use extruded monoliths with straight channels with rectangular cross-section. The model then applies a three-dimensional flow field description coupled with detailed reaction mechanisms and an enthalpy governing equation that includes a heat conducting channel wall.
The inner walls of the single channels of extruded monoliths are frequently coated with a thin layer of washcoat to enlarge the surface. Here, diffusion of reactants and products to and from the catalytic active centers in the washcoat can limit the total heterogeneous reaction rate [8]. Therefore, a set of one-dimensional reaction-diffusion equations is applied to account for washcoat diffusion in the numerical simulation of the monolithic catalyst.

As an example we will discuss experiments and numerical simulations carried out for the partial oxidation of methane to synthesis gas on a rhodium coated extruded monolith.

2. EXPERIMENTAL

The experimental set up was designed in a way that allows the application of detailed models for the physical and chemical processes occurring in the reactor. Experiments were carried out in a tubular quartz reactor, 25 cm long and 2.6 cm in (inner) diameter. The tube contains a 1cm long extruded monolith with a well-defined rectangular cross-section (1mm x 1mm) of its channels. The ceramic monolith made of cordierite is coated with the noble metal rhodium by saturation with an acidic aqueous solution of Rh2(SO4)3, 24 hours drying at 100°C, reduction in H2 at 500°C, and calcination in air at 500°C for 18 hours. Metal loadings are 1 to 3% Rh by weight. Energy dispersive X-ray spectroscopy (EDX) pictures revealed that no sulfur compounds are left on the surface from the impregnation process. For the investigation of washcoat diffusion, cordierite monoliths pre-coated with an alumina washcoat are used.

The entire reactor can be run either auto-thermally or temperature-controlled by a furnace. The gas temperature at the exit of the catalytic monolith is determined by a thermocouple placed inside a thin quartz tube to prevent catalytic reactions. Because of heat losses to the ambience, the measured exit temperature was always significantly lower than the adiabatic reactor temperature would be.

![Fig. 1. Effect of methane/oxygen ratio on selectivity, conversion, and peak (simulation) and outlet temperature; symbols = experiment, lines = simulation. No washcoat is used.](image-url)
The product composition is determined by gas chromatography (TCD, FID) and by quadrupole mass spectroscopy. The latter one can also be used for transient measurements, for instants for studies of ignition and extinction phenomena. The reactor is operated at atmospheric pressure (1.1 bar). The total feed flow rate corresponds to a residence time of few milliseconds.

Methane/oxygen mixtures were fed diluted by argon. In the experiment, we have been studying the effect of composition, flow rate, dilution, and preheat on selectivity and conversion. Exemplary, Fig. 1 exhibits selectivity, conversion, and outlet temperature as function of the methane/oxygen ratio. A good agreement is shown between experimentally determined and numerically predicted data, the latter achieved by the model discussed below.

3. MODELING THE MONOLITH CHANNEL

Even though the experimental measurements reveal that significant heat loss occurs, we simply assume for the model that every channel of the monolith behaves essentially alike. Thus radial profiles over the monolith as a whole are neglected, and only one single channel has to be analyzed. The flow within these small diameter channels is laminar. Because an objective of this study is an appropriate agreement between experimental configuration and flow field model, we solve the three-dimensional Navier-Stokes equations for the simulation of the rectangular shaped channel. These equations are coupled with an energy conservation equation and an additional conservation equation for each chemical species. The energy conservation equation accounts for heat transport by convection and conduction in the gas phase, heat release due to chemical reactions in the gas phase and on the catalytic surface, and heat conduction in the channel walls. Furthermore, we added an external heat loss term at the outer boundary of the channel wall to account for the experimentally occurring heat loss. The temperature-dependent external heat loss was specified so that the predicted outlet temperature agrees with the experimentally measured temperature. Because selectivity and conversion in catalytic partial oxidation of light alkanes strongly depend on the spatial temperature profile, the detailed description of the energy balance is crucial for the understanding of the reaction.

The chemical reactions are modeled by detailed reaction schemes for homogeneous as well as heterogeneous reactions. In the heterogeneous reaction model we apply the mean field approximation. That means that the adsorbates are assumed to be randomly distributed on the surface, which is viewed as being uniform. The state of the catalytic surface is described by the temperature $T$ and a set of surface coverages $\Theta_i$, both depending on the macroscopic position in the reactor, but averaging over microscopic local fluctuations. Balance equations are established to couple the surface processes with the surrounding reactive flow. The production rates $\dot{s}_i$ of surface and gas phase species (due to adsorption and desorption) is then written as

$$\dot{s}_i = \sum_{k=1}^{K_i} v_{ki} k_{fi} \prod_{j=1}^{N_y + N_s} (c_j) v_{ij}$$

(1)
with \( K_i \) = number of surface reactions including adsorption and desorption, \( \nu_i, \nu'_i \) = stoichiometric coefficients, \( k_{ji} \) = forward rate coefficient, \( N_g (N_a) \) = number of gaseous (surface) species, \( c_i \) = concentration of species \( i \), which is given in \( \text{mol cm}^{-2} \) for adsorbed species. Because the binding states of adsorption on the surface vary with the surface coverage of all adsorbed species, the expression for the rate coefficient becomes complex:

\[
k_{ji} = A_k T^{\beta_k} \exp \left[ \frac{-E_{\mu_i}}{RT} \right] \prod_{i=1}^{N_g} \exp \left[ \frac{E_{\mu_i}}{RT} \Theta_i \right]
\]

(2)

with \( A_k \) = preexponential factor, \( \beta_k \) = temperature exponent, and \( E_{\mu_i} \) = activation energy of reaction \( k \). Coefficients \( \mu_{\mu_i} \) and \( \epsilon_{\epsilon_{\mu_i}} \) describe the dependence of the rate coefficients on the surface coverage of species \( i \). For adsorption reactions, sticking coefficients are commonly used. They are converted to conventional rate coefficients by

\[
k_{\text{ads}} = \frac{S_i^0 \sqrt{RT}}{\Gamma \sqrt{2\pi M_i}}
\]

(3)

with \( S_i^0 \) = initial sticking coefficient, \( \Gamma \) = surface site density in \( \text{mol cm}^{-2} \), \( \tau \) = number of sites occupied by the adsorbing species, \( M_i \) = molar mass of species \( i \). While the surface site density can be estimated from the catalyst material, the knowledge of the ratio of the active catalytic surface area to geometrical surface area is essential for the model. An exact value for this ratio has to be determined experimentally. In the simulation discussed here we simply use a value of unity, and the surface site density for rhodium is set to be \( 2.7 \times 10^{-9} \text{ mol cm}^{-2} \).

In spite of numerous surface science studies on \( \text{H}_2, \text{CO} \) and hydrocarbon oxidation there is still a substantial lack in kinetic data. Nevertheless, several surface reaction mechanisms with associated rate expressions have been published for complete and partial oxidation on noble metal catalysts in the last decade. Even though the mechanisms are often based on few experimental data, which were achieved for a limited range of conditions, they led to a better understanding of the process.

In the present study, the surface chemistry is described by a detailed surface reaction mechanism that is under development for the description of partial as well as complete oxidation of methane on rhodium [9]. The mechanism consists of 38 reactions among 6 gas phase species and further 11 adsorbed species, as shown in Table 1. Because the surface coverage is low for the conditions chosen in the present study, the dependence of the rate coefficients on the surface coverage was neglected. However, it may become important at different conditions. For more details, we refer to a forthcoming paper in which the establishment of the reaction mechanism will be discussed [9]. We would like to note that the present study does not focus on the development of the surface reaction mechanism but rather
on its application in multi-dimensional simulations that allow to describe the reactor behavior as adequate as possible.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Balanced Equation</th>
<th>$A$</th>
<th>$E_{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$H_2 + 2\text{Rh}(s) \Rightarrow 2\text{H}(s)$</td>
<td>$1.00 \cdot 10^{-02}$</td>
<td>s.c.</td>
</tr>
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<td>(2)</td>
<td>$O_2 + 2\text{Rh}(s) \Rightarrow 2\text{O}(s)$</td>
<td>$1.00 \cdot 10^{-02}$</td>
<td>s.c.</td>
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<td>(3)</td>
<td>$\text{CH}_4 + \text{Rh}(s) \Rightarrow \text{CH}_4(s)$</td>
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<td>s.c.</td>
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<td>$\text{H}_2\text{O} + \text{Rh}(s) \Rightarrow \text{H}_2\text{O}(s)$</td>
<td>$1.00 \cdot 10^{-01}$</td>
<td>s.c.</td>
</tr>
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<td>(5)</td>
<td>$\text{CO}_2 + \text{Rh}(s) \Rightarrow \text{CO}_2(s)$</td>
<td>$1.00 \cdot 10^{-05}$</td>
<td>s.c.</td>
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<tr>
<td>(6)</td>
<td>$\text{CO} + \text{Rh}(s) \Rightarrow \text{CO}(s)$</td>
<td>$5.00 \cdot 10^{-01}$</td>
<td>s.c.</td>
</tr>
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<td>(7)</td>
<td>$2\text{H}(s) \Rightarrow 2\text{Rh}(s) + \text{H}_2$</td>
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<td>(8)</td>
<td>$2\text{O}(s) \Rightarrow 2\text{Rh}(s) + \text{O}_2$</td>
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<td>(9)</td>
<td>$\text{H}_2\text{O} + \text{Rh}(s) \Rightarrow \text{H}_2\text{O}(s) + \text{Rh}(s)$</td>
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<td>(11)</td>
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<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
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<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
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<td>100.0</td>
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<td>(26)</td>
<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
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<td>68.0</td>
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<td>(27)</td>
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<td>21.0</td>
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<td>(28)</td>
<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
<td>$3.70 \cdot 10^{+21}$</td>
<td>172.8</td>
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<td>(29)</td>
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<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
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<td>(35)</td>
<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
<td>$3.70 \cdot 10^{+21}$</td>
<td>30.1</td>
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<td>(36)</td>
<td>$\text{O}(s) + \text{H}(s) \Rightarrow \text{OH}(s) + \text{Rh}(s)$</td>
<td>$3.70 \cdot 10^{+21}$</td>
<td>145.5</td>
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The units of $A$ are given in terms of [mol, cm, s] and of $E_{a}$ in [kJ/mol]. s.c. = initial sticking coefficient.

If the inner walls of the single channels are coated with a thin layer of washcoat the catalytic active surface area can easily be increased by a factor of $10^{2}$-$10^{3}$ in comparison to the geometrical surface area of the inner wall of the monolith channel. Diffusion and reaction
within the washcoat pores leads to local concentration gradients that have to be resolved to calculate the total heterogeneous reaction rate. Therefore, we apply a set of one-dimensional reaction-diffusion equations to calculate the species concentrations and surface coverages within the washcoat as function of the distance \((r)\) from the gas-washcoat interface:

\[
\frac{\partial j_i}{\partial r} - \gamma \dot{s}_i = 0 .
\]  

(4)

Here, \(\dot{s}_i\) = local molar reaction rate of gas phase species \(i\) due to adsorption and desorption, \(\gamma = \) active catalytic surface area / washcoat volume, \(j_i = \) mass diffusion flux of species \(i\). Depending on the washcoat structure molecular or Knudsen diffusion coefficients have to be used. The number of coupled nonlinear reaction-diffusion equations equals the number of gas phase species. In addition to this equation set, one additional algebraic equation, \(\dot{s}_i = 0\), has to be solved for each surface species. The equation simply says that the surface coverage has to be constant when the steady state is reached.

The numerical simulation is based on the computational fluid dynamics code FLUENT [10] which was coupled to the chemistry tool DETCHEM [5, 11] via FLUENT’s interface for user defined subroutines. DETCHEM models the chemical processes in the gas phase and on the surface including the surface coverage calculation based on multi-step chemical reaction mechanisms. Additionally, several washcoat models can be included [12]. Due to symmetry, only an eighth of the channel cross section has to be simulated, for numerical reasons we simulated a quarter instead.

4. RESULTS AND DISCUSSION

The single channel of the catalytic monolith is simulated under conditions as chosen in the experiment. The methane/oxygen mixture, diluted by 75 vol.% argon, flows at 300 K and 1.1 bar with a uniform velocity of 0.26 m/s (corresponding to 7 slpm over the whole monolith) in the rectangular shaped monolith channel. The simulated channel is 1.1 cm in length with the first millimeter being non-catalytic. In the simulation and in the experiment, the reaction has to be ignited. In the experiment the reactor is inside a furnace which is heated up to initiate the reaction; after ignition the furnace is switched off, the reactor is operated auto-thermally. In the simulation, the channel wall is given a sufficiently high temperature to ignite the reaction. Then, a heat conducting wall is assumed including external heat loss.

In Figure 1, a good agreement is shown between experimentally determined and computed selectivity and conversion. The syngas selectivity and methane conversion are lower than the data reported by the Schmidt group [1] due to significant heat loss in the reactor. The computed peak temperature is much higher than the exit temperature, not only due to heat loss but also due to endothermic steam reforming.

The three-dimensional simulation including the detailed reaction mechanisms allows us to study this behavior in more detail. In previous studies [5], we used the surface reaction mechanism proposed by Hickman and Schmidt in their pioneering work in 1993 [1], in which
steam and CO\textsubscript{2} reforming is not significant. Because of new experimental studies \cite{9}, at least steam reforming seems to be an important reaction step. Among other reasons, this fact led to the development of the revised reaction mechanism. In Figure 2, the profiles of the species mass fractions for a CH\textsubscript{4}/O\textsubscript{2} vol. ratio of 1.8 reveal fast O\textsubscript{2} consumption at the catalyst leading edge while CH\textsubscript{4} is consumed over almost the whole length of the reactor. Complete oxidation takes place at the catalyst entrance only, where O\textsubscript{2} is still available. Because CH\textsubscript{4} as well as re-adsorbed H\textsubscript{2}O decompose into atoms on the surface (Table 1), it cannot be distinguished between direct partial oxidation of CH\textsubscript{4} to H\textsubscript{2} or steam reforming. At least further downstream H\textsubscript{2} is formed via steam reforming only. In contrast to that, CO\textsubscript{2} reforming does not occur. The temperature profiles exhibit the strong axial and radial gradients due to chemical reactions and heat transport.

Fig. 2. Species mass fractions and temperature in the monolith channel (1 mm x 1mm). The contour plots represent the diagonal face of the simulated channel section reaching from the inner corner of the catalytic walls to the channel axis; the diagonal coordinate has been enlarged for visual clarity, the total length is 1.1 cm with the first millimeter being non-catalytic (no wall is shown). The lower right figure shows the temperature profiles in the channel wall, the inlet, and the front symmetry face at the catalyst entrance.
The simulation also reveals that chemical reactions in the gas phase are not significant at atmospheric pressure but become important above 10 bar.

If the monolith is coated with an alumina washcoat, the diameters of the pores are on the order of micrometers. Molecular diffusion inside the pores can limit the overall reaction rate. In Figure 3, we exemplary show computed concentration and coverage profiles inside the washcoat at one millimeter behind the catalyst entrance. Here most of the oxygen is already consumed, and also the oxygen concentration inside the washcoat decreases rapidly due to catalytic reaction with methane. Deeper inside the pores, oxygen is vanished and water reacts with methane to form syngas and carbon dioxide. This behavior explains why the product water shows its highest concentration at the washcoat inlet.

Fig. 3. Species concentrations (left) and surface coverage (right) inside the washcoat. Washcoat parameter: thickness = 100 μm, porosity = 0.51, tortuosity = 3, γ = 10^5 m^-1.

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