

equation system:

$$\frac{\partial(r\rho u)}{\partial z} + \frac{\partial(r\rho v)}{\partial r} = 0 \quad (1)$$

$$\frac{\partial(r\rho u Y_i)}{\partial z} + \frac{\partial(r\rho v Y_i)}{\partial r} = -\frac{\partial}{\partial r}(r j_i) + r \dot{\omega}_i \quad (2)$$

$$\frac{\partial(r\rho u u)}{\partial z} + \frac{\partial(r\rho v u)}{\partial r} = -r \frac{\partial p}{\partial z} + \frac{\partial}{\partial r} \left(\mu r \frac{\partial u}{\partial r} \right) \quad (3)$$

$$\frac{\partial(r\rho u h)}{\partial z} + \frac{\partial(r\rho v h)}{\partial r} = r u \frac{\partial p}{\partial z} + \frac{\partial}{\partial r} \left(\lambda r \frac{\partial T}{\partial r} \right) - \frac{\partial}{\partial r} \left(\sum_i r j_i h_i \right) \quad (4)$$

In these equations ρ [kg m⁻³] indicates the mass density of the mixture, u [m s⁻¹] the axial and v [m s⁻¹] the radial velocity, r [m] the radial and z [m] the axial coordinate, Y_i the mass fraction of species i , $\dot{\omega}_i$ [mol m⁻³ s⁻¹] the chemical source term due to gas-phase reactions, j_i [kg m⁻² s⁻¹] the diffusive flux, μ [kg m⁻¹ s⁻¹] the viscosity, T [K] the temperature, h_i [J kg⁻¹] the enthalpy of species i , and λ [W m⁻¹ K⁻¹] the thermal conductivity. The transport coefficients (μ , λ) and the species diffusion fluxes j_s depend on temperature and species composition.

Chemical reactions on the catalytic reactor wall lead to the following boundary condition:

$$j_i + \rho Y_i v_{St} = \eta F_{cat/geo} \dot{s}_i M_i \quad (5)$$

Here, \dot{s}_i [mol m⁻² s⁻¹] is the source rate of species i by adsorption and desorption processes, M_i [kg mol⁻¹] is the molar mass of species i , j_i [kg m⁻² s⁻¹] is the diffusive flux on the surface, Y_i is the mass fraction of species i in the gas phase adjacent to the surface, v_{St} [m s⁻¹] is the Stefan velocity, and η is the effectiveness factor for diffusion within the washcoat. In this work, the effectiveness factor was fixed to be $\eta = 1$ due to the thin washcoat layer of approximately 15 μ m applied. $F_{cat/geo}$ is used to model the amount of catalyst exposed to the gas phase and describes the ratio of catalytic to geometric surface area; a value of $F_{cat/geo} = 143$ as found by chemisorption measurements for the catalyst used in the present study.

The mean field approximation is applied for modeling the surface reactions [37]. This approximation assumes the adsorbed species to be randomly distributed on a uniform surface, described as a function of temperature and coverage that depends only on the macroscopic position on the catalyst. Fluctuations in coverage are averaged on a microscopic scale.

Due to the high temperature, reactions may also occur in the gas phase. Mass transport (molecular diffusion) between the bulk fluid and the walls of the channel then also becomes significant to understand the interaction between surface and gas-phase reactions. The chemical source terms for gas-phase species (Eqs. (8) and (9)) and for the adsorbed species (Eq. (9)) are given by

$$\dot{\omega}_i = \sum_{k=1}^{K_s} \nu_{ik} k_k \prod_{j=1}^{N_s} c_j^{\nu_{jk}} \quad \text{and} \quad (8)$$

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_k^{(s)} \prod_{j=1}^{N_s+N_c} (c_{sj}^{(s)})^{\nu_{jk}} \quad (9)$$

where K_s is the number of surface reactions, ν_{ik} (product side minus educt side) and ν_{jk} (educt side of the reaction equation) are the stoichiometric coefficients, k_k , $k_k^{(s)}$ [mol.m.s] are rate coefficient (on the surface), N_s is the number of species on the surface, N_g is the number of species in the gas phase, c_{sj} [mol m⁻²] is the surface concentration, that is the product of surface coverage, Θ_j , and surface site density, Γ [37,38]. The surface site density of $\Gamma = 2.77$

$\times 10^{-9}$ mol/cm² was estimated for rhodium (1.67×10^{15} atoms/cm² [39]). Since the experiments were performed under steady-state conditions, Eq. (9) must obey the condition $\dot{s}_i = 0$ for every adsorbed species.

The temperature dependence of the rate coefficients are described by a modified Arrhenius expression:

$$k_k = A_k T^{\beta_k} \exp \left[\frac{-E_{ak}}{RT} \right] \prod_{l=1}^{N_s} (\Theta_l)^{\nu_{lk}} \exp \left[\frac{E_{lk} \Theta_l}{RT} \right], \quad (10)$$

which is extended by an additional factor (product term in Eq. (10)) in case of surface reactions. This extension accounts for the dependence of the rate coefficients on the coverage using the parameters ν_{lk} and E_{lk} [37,38]. The rate coefficient for an adsorption is calculated from initial sticking coefficients S_i^0 by

$$k_i^{(s)} = \frac{S_i^0}{\Gamma \tau} \sqrt{\frac{RT}{2\pi M_i}} \quad (11)$$

where τ is the number of occupied adsorption sites of species i .

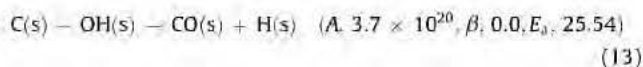
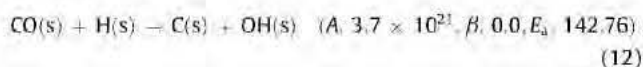
For the numerical solution of the equation system the computer code DETCHEM^{CHANNEL} [40,41] was applied. Given the inlet conditions, the boundary-layer equations are solved in a single sweep of integration along the axial direction by a method-of-lines procedure. The radial derivatives are discretized by a finite-volume method. The resulting differential-algebraic equation system is integrated using the semi-implicit extrapolation solver LIMEX [42].

4. Reaction mechanisms

4.1. Surface reactions

The development of the surface reaction mechanism for steam reforming of natural gas proceeded over several steps. The new mechanism is based on mechanisms previously developed in our group for autothermal reforming (also known as oxidative steam reforming) [43] and partial oxidation [33] of methane over Rh. The autothermal reforming mechanism extends the latter one by introducing four additional reactions of surface-adsorbed HCO. HCO was suggested by Yan et al. [44] to play a crucial role in reforming reactions. The reaction rate constants were calculated by Hei et al. [31] with the UBI-QEP method [45,46].

In this work, further extensions were conducted to enable adequate modeling of steam reforming; aside from minor modifications of rate constants, the reduction of CO(s) by H(s) and the reverse reaction, oxidation of C(s) by OH(s) [31], was included:



The mechanism with the associated reaction rate constants is listed in Table 1.

The conversion of each higher alkane is modeled as global step since no theoretical data has been published yet which could be used for elementary steps. Only C₁-products were detected during the catalytic experiments, so the addition of further steps is neither possible nor necessary. So adsorption of higher alkanes, C₂₊, is treated in a very simple way by one-step dissociative adsorption yielding carbon and hydrogen atoms on the surface. As rate law of