Computational Fluid Dynamics Simulation of Catalytic Reactors

O. Deutschmann

6.6.1 Introduction

Catalytic reactors are generally characterized by the complex interaction of various physical and chemical processes. Monolithic reactors can serve as example, in which partial oxidation and reforming of hydrocarbons, combustion of natural gas, and the reduction of pollutant emissions from automobiles are frequently carried out. Figure 1 illustrates the physics and chemistry in a catalytic combustion monolith that glows at a temperature of about 1300 K due to the exothermic oxidation reactions. In each channel of the monolith, the transport of momentum, energy, and chemical species occurs not only in flow (axial) direction, but also in radial direction. The reactants diffuse to the inner channel wall, which is coated with the catalytic material, where the gaseous species adsorb and react on the surface. The products and intermediates desorb and diffuse back into the bulk flow. Due to the high temperatures, the chemical species may also react homogeneously in the gas phase. In catalytic reactors, the catalyst material is often dispersed in porous structures like washcoats or pellets. Mass transport in the fluid phase and chemical reactions are then superimposed by diffusion of the species to the active catalytic centers in the pores. The temperature distribution depends on the interaction of heat convection and conduction in the fluid, heat release due to chemical reactions, heat transport in the solid material, and thermal radiation. If the feed conditions vary in time and space and/or heat transfer occurs between the reactor and the ambience, a non-uniform temperature distribution over the entire monolith will result, and the behavior will differ from channel to channel.

Today, the challenge in catalysis is not only the development of new catalysts to synthesize a desired product, but also the understanding of the interaction of the catalyst with the surrounding reactive flow field. Sometimes, the exploitation of these interactions can lead to
the desired product selectivity and yield. Hence, it is not surprising that a report on chemical industrial technology in the year 2020 [1] has identified a better understanding of gas-solid flows in chemical reactors as a critical need, and calls for the development of reliable simulation tools that integrate detailed models of reaction chemistry and computational fluid dynamics (CFD) modeling of macro-scale flow structures.

Computational fluid dynamics is able to predict very complex flow fields, even combined with heat transport, due to recently developed numerical algorithms and the availability of faster and bigger (memory) computer hardware. The consideration of detailed models for chemical reactions, in particular for heterogeneous reactions, however, is still very challenging due to the large number of species mass conservation equations, their highly non-linear coupling, and the wide range of time scales introduced by the complex reaction networks.

This chapter introduces the application of CFD simulations to obtain a better understanding of the interactions between mass and heat transport and chemical reactions in catalytic reactors. Concepts for modeling and numerical simulation of catalytic reactors are presented, which describe the coupling of the physical and chemical processes in detail. The ultimate objective of these approaches is to understand and, eventually, to optimize the behavior of the catalytic reactor. Though computational fluid dynamics covers a wide range of problems, reaching from the simulation of the flow around airplanes to laminarization of turbulent flows entering a micro channel, this chapter focuses on the principal ideas and the potential applications of CFD in heterogeneous catalysis; textbooks and specific literature are frequently referenced for more details. It should also be mentioned that the limiting space does not allow the review of all studies, which led to much progress in simulation of catalytic reactors in the last decade.
6.6.2 Modeling of reactive flows

6.6.2.1 Governing equations of multi-component flows

As long as a fluid can be treated as a continuum, the most accurate description of the flow field of multi-component mixtures is given by the transient three-dimensional (3D) Navier-Stokes equations coupled with the energy and species governing equations, which will be summarized in this chapter. More detailed introductions into fluid dynamics and transport phenomena can be found in a number of textbooks \cite{2, 6}. The recently published textbook by Kee et al. \cite{2} also emphasizes on the coupling of flow fields with heterogeneous reactions. Other alternative concepts such as Lattice-Boltzmann models have also been discussed for simulation of catalytic reactors as introduced in Section 6.6.5.1.

Governing equations, which are based on conservation principles, can be derived by consideration of the flow within a certain spatial region, which is called the control volume.

The principle of mass conservation leads to the mass continuity equation

\[ \frac{\partial \rho}{\partial t} + \frac{\partial (\rho v_i)}{\partial x_i} = S_m, \tag{1} \]

with \( \rho \) being the mass density, \( t \) the time, \( x_i \) \((i=1,2,3)\) are the Cartesian coordinates, and \( v_i \) the velocity components. The source term \( S_m \) vanishes unless mass is either deposited on or ablated from the solid surfaces. The Einstein convention is used here, i.e., whenever the same index appears twice in any term, summation over that index is implied, except if the index refers to a chemical species. The principle of momentum conservation for Newtonian fluids leads to three scalar equations for the momentum components \( \rho v_i \)

\[ \frac{\partial (\rho v_i)}{\partial t} + \frac{\partial (\rho v_i v_j)}{\partial x_j} + \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} = \rho g_i, \tag{2} \]

where \( p \) is the static pressure, \( \tau_{ij} \) is the stress tensor, \( g_i \) are the components of the gravitational acceleration. Gravity, the only body force taken into account, can often be neglected when modeling catalytic reactors. The stress tensor is given as
\[ \tau_{ij} = -\mu \left( \frac{\partial v_j}{\partial x_j} + \frac{\partial v_i}{\partial x_i} \right) + \left( \frac{2}{3} \mu - \kappa \right) \delta_{ij} \frac{\partial v_k}{\partial x_k}. \]  

(3)

Here, \( \kappa \) and \( \mu \) are the bulk viscosity and mixture viscosity, respectively, and \( \delta_{ij} \) is the Kronecker delta, which is unity for \( i=j \), else zero. The bulk viscosity vanishes for low density mono-atomic gases and is also commonly neglected for dense gases and liquids \(^3\). The coupled mass continuity and momentum governing equations have to be solved for the description of the flow field.

In multi-component mixtures, not only the flow field is of interest but also mixing of the chemical species and reactions among them, which can be described by an additional set of partial differential equations. Here, the mass \( m_i \) of each of the \( N_g \) gas-phase species obeys a conservation law that leads to

\[ \frac{\partial (\rho Y_i)}{\partial t} + \frac{\partial (\rho v_i Y_i)}{\partial x_j} + \frac{\partial (j_{i,j})}{\partial x_j} = R_i^{\text{hom}}, \]

with \( Y_i \) is the mass fraction of species \( i \) in the mixture \( (Y_i = m_i/m) \) with \( m \) as total mass, \( R_i^{\text{hom}} \) is the net rate of production due to homogeneous chemical reactions. The components \( j_{i,j} \) of the diffusion mass flux caused by concentration and temperature gradients are often modeled by the mixture-average formulation \(^7\):

\[ j_{i,j} = -\rho \frac{Y_i}{X_i} D_i^M \frac{\partial X_i}{\partial x_j} - \frac{D_i^T}{T} \frac{\partial T}{\partial x_j}. \]

(5)

\( D_i^M \) is the effective diffusion coefficient of species \( i \) in the mixture, \( D_i^T \) is the thermal diffusion coefficient, which is significant only for light species. \( T \) is the temperature. The molar fraction \( X_i \) is related to the mass fraction \( Y_i \) using the species molar masses \( M_i \) by

\[ X_i = \frac{1}{\sum_{j=1}^{N_g} \frac{Y_j}{M_j}} Y_i. \]

(6)
Heat transport and heat release due to chemical reactions lead to spatial and temporal temperature distributions in catalytic reactors. The corresponding governing equation for energy conservation is commonly expressed in terms of the specific enthalpy $h$:

$$\frac{\partial (\rho h)}{\partial t} + \frac{\partial (\rho v_j h)}{\partial x_j} + \frac{\partial j_{q,j}}{\partial x_j} = \frac{\partial p}{\partial t} + v_j \frac{\partial p}{\partial x_j} - \tau_{jk} \frac{\partial v_j}{\partial x_k} + S_h,$$

(7)

with $S_h$ being the heat source, for instance due to thermal radiation. In multi-component mixtures, diffusive heat transport is significant due to heat conduction and mass diffusion, hence

$$j_{q,j} = -\lambda \frac{\partial T}{\partial x_j} + \sum_{i=1}^{N_g} h_i j_{i,j}.$$

(8)

$\lambda$ is the thermal conductivity of the mixture. The temperature is then related to the enthalpy by the definition of the mixture specific enthalpy

$$h = \sum_{i=1}^{N_g} Y_i h_i(T),$$

(9)

with $h_i$ being the specific enthalpy of species $i$, which is a monotonic increasing function of temperature. The temperature is then commonly derived from Eq. (9) for known $h$ and $Y_i$.

Heat transport in solids such as reactor walls and catalyst materials can also be modeled by an enthalpy equation, for instance in the form of

$$\frac{\partial (\rho h)}{\partial t} - \frac{\partial }{\partial x_j} \left( \lambda \frac{\partial T}{\partial x_j} \right) = S_h,$$

(10)

where $h$ is the specific enthalpy and $\lambda$ the thermal conductivity of the solid material. $S_h$ accounts for heat sources, for instance due to heat release by chemical reactions and electric or radiative heating of the solid.

This system of governing equations is closed by the equation of state to relate the thermodynamic variables density $\rho$, pressure $p$, and temperature $T$. The simplest model of this relation for gaseous flows is the ideal gas equation
with the universal gas constant \( R = 8.314 \, \text{J mol}^{-1} \, \text{K}^{-1} \).

The transport coefficients \( \mu, D_i^M, D_i^T, \) and \( \lambda \) appearing in Eqs. (3, 5, 8) depend on temperature and mixture composition. They are derived from the transport coefficients of the individual species and the mixture composition by applying empirical approximations \([2, 3, 5]\), which eventually lead to two physical parameters for each species, a characteristic diameter, \( \sigma_i \) and a characteristic energy, \( \varepsilon_i \), which can be taken from data bases \([8]\).

The specific enthalpy \( h_i \) is a function of temperature and can be expressed in terms of the heat capacity

\[
h_i = h_i(T_{\text{ref}}) + \int_{T_{\text{ref}}}^{T} c_{p,i}(T')dT',
\]

where \( c_{p,i} \) is the specific heat capacity at constant pressure. The specific standard enthalpy of formation \( \Delta h^0_{i,298} \) can be used as integration constant \( h_i(T_{\text{ref}} = 298.15 \, \text{K}, \, p_0 = 1 \, \text{bar}) \).

Experimentally determined and estimated standard enthalpies of formation, standard entropies, and temperature dependent heat capacities can be found in data bases \([9-11]\) or estimated by Benson’s additivity rules \([12]\).

### 6.6.2.2 Turbulent flows

Turbulent flows are characterized by continuous fluctuations of velocity, which can lead to fluctuations in scalars such as density, temperature, and mixture composition. Turbulence can be desired in catalytic reactors to enhance mixing and reduce mass transfer limitations but is also unwanted due to the increased pressure drop and energy dissipation. An adequate understanding of all facets of turbulent flows is still missing \([5, 13, 14]\). In the area of catalytic systems, some progress had been made recently in turbulent flow modeling, e.g. in catalytically stabilized combustion \([15, 16]\). The Navier-Stokes equations as presented above are
in principal able to model turbulent flows (Direct Numerical Simulation). However in practice, the solutions of the Navier-Stokes equations for turbulent flows in technical reactors demand a prohibitive amount of computational time due to the huge number of grid points needed to resolve the small scales of turbulence. Therefore, several concepts were developed to model turbulent flows by the solution of averaged governing equations. However, the equation system is not closed, that means a model has to be set up to describe the so-called Reynold stresses that are the correlations between the velocity fluctuations and the fluctuations of all the quantities of the flow (velocity, enthalpy, mass fractions). The $k - \varepsilon$-model \cite{17} is the currently most widely used concept for modeling the Reynold stresses, which adds two additional partial differential equations for the description of the turbulent kinetic energy, $k$, and the dissipation rate, $\varepsilon$, to the governing equations. Although the model has well-known deficiencies, it is today implemented in most commercial CFD codes and also widely used for the simulation of catalytic reactors. Recently, turbulent flow field simulations are often based on Large-Eddy-Simulation (LES), which combines DNS for the larger scales with a turbulence model, e.g. $k - \varepsilon$-model, for the unresolved smaller scales.

Aside from this closure problem, one still has to specify the averaged chemical reaction rates \cite{5,13}. Due to the strong non-linearity of the rate coefficients (Eq. 14), the source terms of chemical reactions in turbulent flows cannot be computed using average concentrations and temperature. Here, probability density functions (PDFs) \cite{5}, either derived by transport equations \cite{14} or empirically constructed \cite{18}, are used to take the turbulent fluctuations into account when calculating the chemical source terms. For the simulation of reactions on catalysts, it is important to use appropriate models for the flow laminarization at the solid surface.
6.6.2.3 Homogeneous chemical reactions in the gas phase

In many catalytic reactors, the reactions do not exclusively occur on the catalyst surface but also in the fluid flow. In some reactors even the desired products are mainly produced in the gas phase, for instance in the oxidative dehydrogenation of paraffins to olefins over noble metals at short contact times and high temperature \[19-26\]. Such cases are dominated by the interaction between gas-phase and surface kinetics and transport. Therefore, any reactor simulation needs to include an appropriate model for the homogeneous kinetics along with the flow models. The species governing equations (4) contain a source term \(R_{i}^{\text{hom}}\), which is the specific net rate of production of species \(i\) due to homogeneous chemical reactions.

Considering a set of \(K_{g}\) chemical reactions among \(N_{g}\) species \(A_{i}\)

\[
\sum_{i=1}^{N_{i}} v'_{ik} A_{i} \rightarrow \sum_{i=1}^{N_{i}} v''_{ik} A_{i},
\]

with \(v'_{ik}, v''_{ik}\) being the stoichiometric coefficients, and an Arrhenius-like rate expression, \(AT^{\beta} \exp\left(-\frac{E_{a}}{RT}\right)\), this source term can be expressed by

\[
R_{i}^{\text{hom}} = M_{i} \sum_{k=1}^{K_{g}} (v''_{ik} - v'_{ik}) A_{k} T^{\beta_{k}} \exp\left[\frac{-E_{a_{j}}}{RT} \prod_{j=1}^{N_{j}} \left(\frac{Y_{j} \rho}{M_{j}}\right)^{a_{jk}}\right].
\]

Here, \(A_{k}\) is the pre-exponential factor, \(\beta_{k}\) is the temperature exponent, \(E_{a_{j}}\) is the activation energy, and \(a_{jk}\) is the order of reaction \(k\) related to the concentration of species \(j\). Various reliable sets of elementary reactions are available for modeling homogeneous gas phase reactions, for instance for total \(^{5}\) and partial oxidation, and pyrolysis of hydrocarbons. The advantage of the application of elementary reactions is that the reaction orders \(a_{jk}\) in Eq. (14) equal the stoichiometric coefficients \(v'_{jk}\).

Even though the implementation of Eq. (14) is straightforward, an additional highly nonlinear coupling is introduced into the governing equations leading to considerable computational efforts. The nonlinearity, the large number of chemical species, and the fact
that chemical reactions exhibit a large range of time scales make the solution of those equation systems challenging. In particular for turbulent flows, but sometimes even for laminar flows, the solution of the system is too CPU time-consuming with current numerical algorithms and computer capacities. This calls for the application of reduction algorithms for large reaction mechanisms, for instance by the extraction of the intrinsic low dimensional manifolds of trajectories in chemical space \[^{27}\], which can be applied for heterogeneous reactions \[^{28}\]. Another approach is to use “as little chemistry as necessary”. In these so-called adaptive chemistry methods, the construction of the reaction mechanism includes only steps relevant for the application studied \[^{29}\].

### 6.6.3 Modeling surface reaction rates

#### 6.6.3.1 Coupling with the flow field

Depending on the spatial resolution of the catalytic layer the species mass fluxes due to catalytic reactions are differently coupled with the flow field.

In the first case considered the catalytic layer can be resolved in space. Examples are catalytically coated walls in honeycomb structures (Fig. 1), disks, and plates and well-defined porous media (fixed bed reactors, foams, washcoats), in which the shape of the individual pellet or channel is known. The chemical processes at the surface are then coupled with the surrounding flow field by boundary conditions for the species-continuity equations, Eqs. (4), at the gas-surface interface \[^{2,30}\]:

\[
\vec{n}(\vec{j}_i + \rho \vec{v}_{\text{solute}} Y_i) = R_{i}^{\text{het}}
\]

Here \(\vec{n}\) is the outward-pointing unit vector normal to the surface, \(\vec{j}_i\) is the diffusion mass flux of species \(i\) as discussed in Eqs. (4), and \(R_{i}^{\text{het}}\) is the heterogeneous surface reaction rate, which is given per unit geometric surface area, corresponding to the reactor geometry, in kg m\(^{-2}\) s\(^{-1}\).
The Stefan velocity \( \vec{v}_{\text{Stef}} \) occurs at the surface if there is a net mass flux between the surface and the gas phase:

\[
\vec{m}_{\text{Stef}} = \frac{1}{\rho} \sum_{i=1}^{N} R_{i}^{\text{het}}.
\] (16)

At steady-state conditions, this mass flux vanishes unless mass is deposited on the surface, e.g. chemical vapor deposition, or ablated, e.g. material etching. Equation (15) basically means that for \( \vec{v}_{\text{Stef}} = 0 \) the amount of gas-phase molecules of species \( i \), which are consumed/produced at the catalyst by adsorption/desorption, have to diffuse to/from the catalytic wall (Eq. 5). Only for fast transient (< \( 10^{-4} \) s) adsorption/desorption processes, e.g. during ignition of catalytic oxidation, Eq. (15) breaks down and special treatment of the coupling is needed \([31, 32]\).

The calculation of \( R_{i}^{\text{het}} \) requires the knowledge of the amount of catalytically active surface area in relation to the geometric surface area, here denoted by \( F_{\text{cat/geo}} \), at the gas-surface interface:

\[
R_{i}^{\text{het}} = \eta F_{\text{cat/geo}} \dot{s}_{i}
\] (17)

Here, \( \dot{s}_{i} \) is the molar net production rate of gas phase species \( i \), given in mol m\(^{-2}\) s\(^{-1}\); the area now refers to the actual catalytically active surface area. \( F_{\text{cat/geo}} \) can be determined experimentally, e.g. by chemisorption measurements. The effect of internal mass transfer resistance for catalyst dispersed in a porous media is included by the effectiveness factor \( \eta \) \([6, 33]\). More detailed models for transport in porous media are discussed in Section 6.6.4.

In most fixed bed reactors with large numbers of catalytic pellets, for non-trivial shapes of the catalysts, and for catalyst dispersed in porous media, the structure of the catalyst can not be resolved geometrically. In those cases, the catalytic reaction rate is expressed per volumetric unit, that means \( R_{i}^{\text{het}} \) is now given in kg m\(^{-3}\) s\(^{-1}\); the volume here refers to the volume of a
computational cell in the geometrical domain of fluid flow. Then $R_i^{\text{het}}$ simply represents an additional source term on the right side of the species-continuity equation, Eq. (4), and is computed by

$$R_i^{\text{het}} = \eta S_v M \delta_i,$$

where $S_v$ is the active catalytic surface area per volumetric unit, given in m$^{-1}$, determined experimentally or estimated. $F_{\text{cat/geo}}$ as well as $S_v$ can be expressed as function of the reactor position and time to account for in-homogeneously distributed catalysts and loss of activity, respectively. In reactors with more than one catalytic material, a different value for $F_{\text{cat/geo}}$ or $S_v$ can be given for every individual active material or phase, respectively.

### 6.6.3.2 Modeling the surface reaction rate

Since the rate of catalytic reactions is very specific to the catalyst formulation, global rate expressions have been used for many years $^{[6, 34]}$. The reaction rate has often been based on catalyst mass, catalyst volume, reactor volume, or catalyst external surface area. The implementation of this macro kinetic approach is straightforward; the rate $\dot{s}_i$ can easily be expressed by any arbitrary function of gas-phase concentrations and temperature at the catalysts surface calculated at any computational cell containing either catalytically active particles or walls. It is evident that this approach cannot account for the complex variety of phenomena of catalysis and that the rate parameters must be evaluated experimentally for each new catalyst and various external conditions.

Since measuring and modeling surface reaction rates is thoroughly discussed in many Chapters of this Handbook, at this point only the concept of the mean-field approximation is discussed in the remainder of this section. This concept currently is state of the art in CFD modeling of catalytic reactors and implemented in a variety of CFD codes.
A Mean field approximation and reaction kinetics

The mean field approximation is related to the size of the computational cell in the flow field simulation assuming that the local state of the active surface can be represented by mean values for this cell. Hence, this model assumes randomly distributed adsorbates 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 $\theta_i$, that is the fraction of the surface covered with surface species $i$. The surface temperature and the coverages depend on time and the macroscopic position in the reactor, but are averaged over microscopic local fluctuations.

Under those assumptions a chemical reaction can be defined in analogy to Eq. (13) by

$$\sum_{i=1}^{N_i} v_i' A_i \rightarrow \sum_{i=1}^{N_i} v_i'' A_i$$  \hspace{1cm} (19)

The difference is that now the $A_i$ denote not only gas-phase species (e.g., H$_2$) but also surface species (e.g., H(s)) and bulk species (e.g., H(b)). The $N_s$ surface species are those that are adsorbed on the top mono-atomic layer of the catalytic particle while the $N_b$ bulk species are those found in the inner solid catalyst.

Steric effects of adsorbed species and various configurations, e.g., the type of the chemical bonds between adsorbate and solid, can be taken into account using the following concept: The surface structure is associated with a surface site density $\Gamma$ that describes the maximum number of species that can adsorb on a unit surface area, given, e.g., in mol m$^{-2}$. Then each surface species is associated with a coordination number $\sigma_i$ describing the number of surface sites which are covered by this species. Under the assumptions made, a multi-step (quasi-elementary) reaction mechanism can be set up. The molar net production rate $\dot{\theta}_i$ is then given as

$$\dot{\theta}_i = \sum_{k=1}^{K_i} \mu_k' \prod_{j=1}^{N_s + N_b} c_j^{v_i''}.$$  \hspace{1cm} (20)
Here, $K_s$ is the number of surface reactions, $c_i$ are the species concentrations, which are given, e.g., in mol m$^{-2}$ for the $N_s$ adsorbed species and in, e.g., mol m$^{-3}$ for the $N_g$ and $N_b$ gaseous and bulk species. According to Eq. (20) and the relation $\Theta_i = c_i \sigma_i \Gamma^{-1}$, the variations of surface coverages follow

$$\frac{\partial \Theta_i}{\partial t} = \frac{\dot{s}_i \sigma_i}{\Gamma}.$$  \hspace{1cm} (21)

Since the reactor temperature and concentrations of gaseous species depend on the local position in the reactor, the set of surface coverages also varies with position. However, no lateral interaction of the surface species between different locations on the catalytic surface is modeled. This assumption is justified by the fact that the computational cells in reactor simulations are usually much larger than the range of lateral interactions of the surface processes. In each of these cells, the state of the surface is characterized by mean values (mean-field approximation). The set of differential equations (21) has to be solved simultaneously with flow field equations for every computational cell containing catalytic material. At steady state, the left sides of Eqs. (21) become zero, and a set of algebraic equations has to be solved. The time scales to reach the steady state of Eqs. (21) are commonly much shorter than the time scales of significant variations of species concentrations and temperature in the fluid. Therefore, a quasi-steady state assumption with vanishing left sides of Eqs. (21) is frequently justified even for transient reactor operation.

The binding states of adsorption of all species vary with the surface coverage. This additional coverage dependence is modeled in the expression for the rate coefficient $k_i$ in Eq. (20) by two additional parameters, $\mu_i$ and $\epsilon_i$ \cite{2,30}:

$$k_i = A_i T^{\beta_i} \exp \left[ \frac{-E_{Z_i}}{RT} \right] \prod_{i=1}^{N_s} \Theta_i^{\mu_i} \exp \left[ \frac{\epsilon_i \Theta_i}{RT} \right].$$  \hspace{1cm} (22)

For adsorption reactions sticking coefficients are commonly used, which can be converted to conventional rate coefficients \cite{2,35} by
\[
k_{i,s}^{\text{ads}} = \frac{S_i^0}{\Gamma^i} \sqrt{\frac{RT}{2\pi M_i}}, \quad \text{where } \tau = \sum_{j=1}^{N} \nu_{jk}.
\]

\(S_i^0\) is the initial (uncovered surface) sticking coefficient.

**B Development of multi-step surface reaction mechanisms**

The development of a reliable surface reaction mechanism is a complex process following the scheme given in Fig. 2. A tentative reaction mechanism can be proposed based on experimental surface science studies, on analogy to gas-phase kinetics and organo-metallic compounds, and on theoretical studies, increasingly including DFT calculations \([36, 37]\). This mechanism should include all possible paths for the formation of the chemical species under consideration in order to be “elementary-like” and thus applicable over a wide range of conditions. The mechanism idea then needs to be evaluated by numerous experimentally derived data, which are compared with theoretical predictions based on the mechanism. Here, the simulations of the laboratory reactors require appropriate models for all significant processes in order to evaluate the intrinsic kinetics. Sensitivity analysis leads to the crucial steps in the mechanism, for which refined kinetic experiments and data may be needed.

Since the early nineties, many groups have developed surface reaction mechanisms following the concepts discussed above. In particular oxidation reactions over noble metals have been modeled extensively such as of hydrogen \([38-44]\), CO \([45-47]\), and methane \([31, 48-52]\) and ethane \([22, 26, 53, 54]\) over Pt, formation of synthesis gas over Rh \([52, 55]\). Lately, mechanisms have been established for more complex reaction systems, for instance, three-way catalysts \([56]\) or Chemical Vapor Deposition (CVD) reactors for the formation of diamond \([57, 58]\), silica \([59]\), and nanotubes \([60]\). A crucial issue with many of the mechanisms published is thermodynamic consistency. Even though most of the mechanisms lead to consistent enthalpy diagrams, many are not consistent regarding the entropy change in the overall reaction due to missing knowledge on the transition states of the individual reactions and therefore on the pre-
exponentials in the rate equations. Lately, optimization procedures enforcing overall thermodynamic consistency have been applied to overcome this problem \[61\].

C Limitation of the models and alternate approaches

Catalytic surfaces are certainly non-uniform; site heterogeneity exists because the surface of practical catalyst particles is characterized by terraces of different crystal structures, steps, edges, additives, impurities, and defects. In the method (mean-field approximation) discussed above, the site heterogeneity was averaged out by mean rate coefficients. If the distribution of the different types of adsorption sites and the reaction kinetics on those sites are known, the concept discussed can easily be used to set up a reaction mechanism, which consists of several sub-mechanisms for the different surface structures \[30\]. This concept was applied in the framework of a two-adsorption site model for the simulation of CO combustion on polycrystalline Pt \[62\]. The site heterogeneity can be described by the probability that an arbitrary site is characterized by the associated reaction kinetics. In the models discussed so far, this probability function is a sum over a finite number of surface structures, but also continuous functions are used in literature \[63\]. Here, the problem again is the limited knowledge of the distribution of the different types of surface patches and the kinetics on these patches.

Effects resulting from lateral interactions of the adsorbates are inherently more difficult to treat. In the mean-field approximation they are either neglected or incorporated by mean rate coefficients. If the specific adsorbate-adsorbate interactions are understood quantitatively, then a Monte Carlo (MC) simulation of the surface chemistry can be carried out \[64\]. MC simulations at various temperatures and gas-phase concentrations lead to apparent activation energies and reaction orders. In catalytic combustion, a real time-dependent MC simulation including the surrounding flow field was recently carried out for CO oxidation on Pt and compared with simulations using the mean-field approximation \[65\]. Even though MC
calculations offer great promise for the understanding of complex surface phenomena, the
application of these calculations to more complex reaction systems and the integration into
CFD simulations is not tractable yet, because of the limited knowledge about the surface
chemistry and due to computational limitations, respectively.

6.6.3.3 Model evaluation
The coupling of several complex models introduces a large number of parameters into the
simulations. For instance, detailed reaction schemes may have hundreds of kinetic parameters,
each value associated with a certain inaccuracy. Hence, agreement between predicted and
experimentally observed overall conversion and selectivity alone is not sufficient to evaluate
individual sub models. Time and locally resolved profiles provide a more stringent test for
model evaluation. Useful data arise from the experimental resolution of local velocity profiles
by laser Doppler anemometry/velocimetry (LDA, LDV)\(^{[15, 66, 67]}\) and of spatial and temporal
species profiles by in situ, non-invasive methods such as Raman and laser induced
fluorescence (LIF) spectroscopy. For instance, an optically accessible catalytic channel
reactor can be used to evaluate models for heterogeneous and homogeneous chemistry as well
as transport by the simultaneous detection of stable species by Raman measurements and OH
radicals by Planar laser-induced fluorescence (PLIF)\(^{[68, 69]}\). Exemplarily, Figure 3 reveals the
onset of homogeneous ignition of methane oxidation in a platinum coated catalytic channel by
monitoring the OH radical distribution. While methane is oxidized catalytically along the
channel walls releasing some OH radicals, at a certain point in the reactor a transition to
homogeneous oxidation occurs accompanied with large OH radical concentrations in the
flame region. Since transient phenomena such as ignition, extinction and oscillations of
reactions are very sensitive to transport and kinetics, they can serve as measurements for a
critical evaluation of theoretical models. For instance, the reliability of different
heterogeneous and homogeneous reaction schemes proposed in literature was investigated by
comparison of the experimentally derived ignition distances with numerical elliptic two-dimensional simulations of the flow field using combinations of a variety of schemes \cite{70-73}. While some models perform well, others lead to quite inaccurate predictions as shown in Fig. 3. Sensitivity analysis of the applied reaction schemes can then reveal the crucial steps. As example for the evaluation of transport models, turbulent flows in catalytic channels are discussed in Chapter 6.6.6.1.

6.6.4 Transport and reactions in porous media

Porous media are present everywhere in catalytic reactors \cite{74, 75}, for instance fixed-bed reactors, catalytic filters, washcoat layers, perforated plates, flow distributors, tube banks, membranes, electrodes, fiber materials etc. Modeling the transport and reactions in the actual tortuous structure on the microscopic level is a rather formidable task. Therefore, it is often necessary only to work with small representative volume elements where the porous medium and other properties are assumed to be homogenized. Several methods have been developed to include porous media and reactions in CFD simulations.

6.6.4.1 Momentum and energy equations for porous media

Most porous media models in CFD codes incorporate an empirically determined flow resistance accounting for the pressure drop, which is a sink in the governing momentum equation (2). In the case of simple homogeneous porous media a source term is added to the right side of Eq. (2),

$$S_i = -\left( \frac{\mu}{\alpha} v_i + \frac{C}{2} \rho |v| v_i \right)$$

(24)

where $\alpha$ is the permeability (Darcy’s law) and $C$ is the inertial resistance, which can be viewed as a loss per unit length along the flow direction. Concerning the temperature profile in porous media, the enthalpy equations (7) and (10) have to be adapted. The total enthalpy is
now a sum of the enthalpies of the fluid and the solid. Their partition is defined by the porosity. An effective thermal conductivity is used based on the porosity and the thermal conductivities of the fluid and the solid. This continuum approach has to be used carefully, for instance the effect of the porous medium on turbulent flows can barely be approximated within this concept. The approach, which assumes constant unidirectional flow, also breaks down for fixed bed reactors with reactor diameter being less than ten times the particle size. Thus the model cannot predict the velocity maximum in the vicinity of the wall observed experimentally for those reactors \cite{76}. An averaged velocity with a radial varying axial component can be provided by a further modification of the momentum balance \cite{76-78} as improvement of the classical model.

6.6.4.2 Reaction-diffusion equation

The dispersion of the catalyst material in porous layers or pellets easily leads to a reduced overall reaction rate due to finite diffusion of the reactants to and products from the active sites. The simplest model to account for this mass transport limitation is the effectiveness factor $\eta$ as introduced in Eq. (17). The effectiveness factor is analytically calculated via the Thiele module taking into account the thickness of the porous medium, the species concentrations at the fluid/washcoat interface, an effective diffusion coefficient, and the ratio of the catalytic surface area to the washcoat volume. Since mass conservation has to be obeyed, the same effectiveness factor must be applied for all chemical species. Therefore, this model fails at conditions at which the reaction rate and diffusion coefficient of more than a single species determines overall reactivity. Like in this case, the interaction of diffusion and reaction demands better models if mass transport in the porous media is dominated rather by diffusion than by convection.

Concentration gradients inside the porous media result in spatial variations of the surface reaction rates $\dot{s}_r$. In thin catalyst layers (washcoats), these are primarily significant in normal
direction to the boundary fluid/washcoat. Therefore, one-dimensional reaction-diffusion equations are applied with their spatial coordinate in that direction. Each chemical species leads to one reaction-diffusion equation, which is written in steady state as

$$\frac{\partial}{\partial r} \left( -D_{i}^{\text{eff}} \frac{\partial c_{i}^{W}}{\partial r} \right) - S_{i} \dot{s}_{i} = 0. \quad (25)$$

Here, $c_{i}^{W}$ denotes the species concentration in the washcoat in normal direction to the boundary fluid/washcoat. $D_{i}^{\text{eff}}$ is the effective diffusion coefficient, which can account for the different diffusion processes in macro and micro pores and can be derived from the binary diffusion coefficients \cite{75, 79}. In addition to Eq. (25), the surface coverages are calculated using Eq. (21), in which the left side vanished at steady state.

A heat balance, in which Eqs. (7) and (10) are combined, may be added to the model to account for temperature variations in the porous media. Since Eq. (25) is only applicable for thin catalytic layers or small pellets without net mass fluxes (ablation, deposition etc.) and internal pressure driven flows, temperature variations can generally be neglected. Eq. (25) is coupled with the surrounding flow field, Eq. (5), at the interface between open fluid and catalytic layer/pellet, where the diffusion fluxes normal to this interface must compensate.

In this model the species concentrations, catalytic reaction rates, and surface coverages do not only depend on the position of the catalytic layer/pellet in the reactor, but also vary inside the catalyst layer/particle leading to time consuming computations.

6.6.4.3 Dusty-Gas Model

Fluxes within porous media which are driven by gradients in concentration and pressure, i.e. diffusion and convection, can be described by the Dusty Gas Model (DGM) \cite{75, 79}. This model, which is also applicable for three-dimensional and larger porous media, is superior to the ones discussed in the two previous sections but also leads to more sophisticated
computational efforts. The conservation equation (4) for reactive porous-media species transport at steady state is now written as

$$\frac{\partial (j_{i,j})}{\partial x_j} = R_{i}^{\text{hom}} + R_{i}^{\text{het}} = R_{i}^{\text{hom}} + S_i M_j \delta_j .$$  \hspace{1cm} (27)

The components $j$ of the gas-phase mass fluxes, $j_{i,j}$, of species $i$ are evaluated by an implicit relationship among the molar concentrations, concentration gradients, and pressure gradients \cite{75, 79}:

$$j_{i,j} = \left[ - \sum_{l=1}^{N} D_{il}^{\text{DGM}} \frac{\partial c_i}{\partial x_j} - \left( \sum_{l=1}^{N} D_{il}^{\text{DGM}} \frac{c_i}{D_{il}^{\text{eff}}} \right) \frac{\partial p}{\mu \partial x_j} \right] M_j .$$ \hspace{1cm} (27)

Here $D_{il}^{\text{DGM}}$ are the DGM diffusion coefficients and $D_{il}^{\text{eff},\text{Kn}}$ are the effective Knudsen diffusion coefficients. The first term on the right hand side of Eq. (27) represents the diffusive flux and the second the viscous flux. The DGM diffusion coefficients can be represented as a matrix inverse $D_{il}^{\text{DGM}} = H^{-1}$, where the elements of the $H$ matrix are given by

$$h_{ij} = \frac{1}{D_{ij}^{\text{eff},\text{Kn}}} + \sum_{j \neq i} \frac{X_j}{D_{ij}^{\text{eff}}} \delta_{ij} + (\delta_{ij} - 1) \frac{X_j}{D_{ij}^{\text{eff}}} .$$ \hspace{1cm} (28)

The effective binary diffusion coefficients $D_{il}^{\text{eff}}$ in the porous media are related to the ordinary binary diffusion coefficient $D_{il}$ by

$$D_{il}^{\text{eff}} = \frac{\Phi \tau_g}{\tau_g} D_{il} ,$$ \hspace{1cm} (29)

with $\Phi = \text{porosity}$ and $\tau_g = \text{tortuosity}$. The effective Knudsen diffusion coefficient can be expressed as

$$D_{il}^{\text{eff},\text{Kn}} = \frac{4 \Phi \tau_g}{3 \tau_g} r_p \sqrt{\frac{8RT}{\pi M_i}} ,$$ \hspace{1cm} (30)

where $r_p$ is the average pore radius.
A critical evaluation of transport models including DGM and the development of a more general concept have been proposed by Kerkhof [80, 81].

6.6.5 Numerical methods and computational tools

There are a variety of methods to solve the coupled system of partial differential and algebraic equations (PDE), which were presented in the previous section for modeling catalytic reactors. Very often, the transient three-dimensional governing equations are simplified (no time dependence, symmetry, preferential flow direction, infinite diffusion etc.) as much as possible, but still taking care of all significant processes in the reactor. Simplifications often are not straight-forward and need to be conducted with care. Special algorithms were developed for special types of reactors to achieve a converged solution or to speed up the computation solution.

6.6.5.1 Numerical methods for the solution of the governing equations

An analytic solution of the PDE system is only possible in very limited special cases; for all practical cases, a numerical solution is needed. Numerical solution means that algebraic equations are derived that approximate the solution of the PDE system at discrete points of the geometrical space of the reactor. The way of selection of these grid points and the derivation of algebraic equations, which are finally solved by the computer, are called discretization. Since the solution of the discretized equations is only an approximation of the solution of the PDE system, an error analysis is an essential feature of the interpretation of every CFD simulation.

The three major methods of discretization [82] are the methods of Finite Differences (FDM), Finite Volumes (FVM), and Finite Elements (FEM). The simplest method is FDM, which is based on a Taylor series expansion of the solution vector between neighboring grid points and applied for well structured grids. The chosen number of terms of the Taylor series determines
the accuracy. In contrast to FDM, the Finite Volume method can be applied for unstructured grids so that for regions with larger gradients more grid points can be chosen, well-adapted to the reactor behavior. FVM calculates the dependent variables not for certain points but for certain volumes. Source terms within cells and fluxes through the boundaries of these cells are considered to derive the local values, which makes this method very physically descriptive and also allows simple error estimation.

The most universal method from a mathematical point of view is FEM [83, 84]; FDM and FVM can be considered as special cases of FEM. FEM originates from structural mechanics and has recently found increased use in CFD. FEM generates the computational grid in a very adaptive way and is therefore ideal for complex geometries. Furthermore, FEM based codes are suited for the application of parallel computers. The great flexibility of FEM regarding the description of the solution and its convergence comes at the cost of a higher complexity of the computer program. Today, all commercial CFD codes are based on the methods FVM or FEM.

Very different from those three methods are the Lattice-Boltzmann methods (LBM) [85], which have recently become popular in particular for the simulation of complex flow structures found in fixed beds [86-88]. The LBM may be considered as a finite difference method for a discrete Boltzmann equation. The method simulates hydrodynamic or mass transport phenomena by tracking the time evolution of particle distribution functions confined to a lattice moving with discrete velocity during discrete advances in time. Each time step is subdivided into separate streaming and collision steps. It could be shown that correctly chosen particle distribution functions recover the Navier–Stokes equations. LBM for reaction engineering applications is still under development; in particular the implementation of heat transport and complex reaction schemes seems to be difficult. There is also no commercial code available yet based on LBM.
6.6.5.2 CFD software

Currently available multi-purpose commercial CFD codes can simulate very complex flow configurations including turbulence and multi component transport based on FVM and FEM. However, CFD codes still have difficulties to implement complex models for the chemical processes. One problem is the insufficient number of reactions and species the codes can handle. An area of recent development is the implementation of detailed models for heterogeneous reactions.

Several software packages have been developed for modeling complex reaction kinetics in CFD such as CHEMKIN [89], CANTERA [90], DETCHEM [91], which also offer CFD codes for special reactor configurations such as channel flows and monolithic reactors. These kinetic packages and also a variety of user written subroutines for modeling complex reaction kinetics have meanwhile been coupled to several commercial CFD codes. Aside from the commercially wide-spread multi-purpose CFD software packages such as FLUENT [92], STAR-CD [93], FIRE [94], CFD-ACE+ [95], CFX [96], a variety of multi-purpose and specialized CFD codes have been developed in academia and at research facilities such as MP-SALSA [97]. The latter ones are often customized for special reactor types and therefore more efficient. Another tool for the solution of PDE systems based on the finite element method is the FEMLAB software package [98], which has recently been applied for CFD simulations of catalytic reactors as well.

6.6.5.3 Solvers for stiff ODE and DAE systems

Model simplification and numerical algorithms make it possible to convert the PDE system of the governing equations to an ordinary differential equation (ODE) system or a coupled system of ODEs and algebraic equations called differential-algebraic equation (DAE) system. In those equation systems, time or one spatial component is the independent variable. Several computer codes have been developed to solve ODE and DAE systems. In particular suitable
for reactive flows are DASSL [99], LSODE [100], LIMEX [101, 102], and VODE [103]. For the underlying theory of the numerical solution of DAE systems and software implementation it is referred to the textbook by Ascher and Petzold [104].

6.6.6 Reactor simulations

In the remainder of this Chapter, recent and challenging CFD simulations of catalytic reactors will be discussed according to the type of reactor.

6.6.6.1 Flow through channels

There is a wide variety of chemical reactors, in which the reactive mixtures flow trough channel-like devices such as tubular chemical reactors, automotive catalytic converters, catalytic-combustion monoliths.

Pipes with diameters ranging from a few centimeters up to meters are one class of those reactors. The flow field here is in most cases turbulent, guaranteeing good mixing of the reactants. A fine resolution of flow field details is rarely of interest, and, aside from that, such a task exceeds today’s computer capacities. Therefore, averaged equations and turbulence models are applied as introduced in Section 6.6.2.2.

Mantzaras et al. [16] applied the $k$-$\varepsilon$ model, a presumed (Gaussian) probability density function for gaseous reactions, and a laminar-like closure for surface reactions to study turbulent catalytically stabilized combustion of lean hydrogen-air mixtures in plane platinum-coated channels. They also examined different low-Reynolds number near-wall turbulence models and compared the numerically predicted results with data derived from planar laser-induced fluorescence measurements of OH radicals, Raman measurements of major species and laser doppler velocimetry measurements of local velocities and turbulence [68]. They found that discrepancies between predictions and measurements are ascribed to the capacity of the
various turbulence models to capture the strong flow laminarization induced by the heat
transfer from the hot catalytic surfaces.

Another class of tube-like reactors is the monolith or honeycomb structure, which consists of
numerous passageways with diameters reaching from a tenth of a millimeter to few
millimeters. The flow field in the thin channels of this reactor type is usually laminar. The
catalytic material is mostly dispersed in a washcoat on the inner channel wall. Monolith
channels are manufactured with various cross-sectional shapes, e.g., circular, hexagonal,
square or sinusodial.

Several recent CFD studies were conducted to understand the impact of the real washcoat
shape on transport and overall reaction rate \[33, 105, 106\]. Hayes et al. \[106\] recently showed that
the internal diffusion resistance, expressed in terms of an effectiveness factor, cannot be
represented in terms of a unique curve using the generalized Thiele modulus approach to
model diffusion and reaction in the washcoat of a catalytic monolith reactor. The most
significant deviation occurs when the washcoat has the greatest variation in thickness.

Three-dimensional Navier-Stokes equations including detailed reaction mechanisms and heat
balances that also account for heat conducting channel walls and external heat loss were used
for the simulation of partial oxidation of methane to synthesis gas on rhodium coated
monoliths with rectangular channel cross-section. The simulation was based on FLUENT
coupled with user defined functions (UDF) to handle the chemistry and transport in the
washcoat \[107\].

Since those 3D simulations require long computing times, the single monolith channel is often
approximated by a perfect cylindrical geometry, even for non-circular cross-sections.
Furthermore, the inlet flow pattern is assumed to follow this geometry. Hence, the flow
through the single channel can be treated as the flow through a tubular reactor that means two-
dimensional (2D) with the axial and radial position as independent variables. The resulting 2D
Navier-Stokes equations still describe an elliptic flow, that means, information in the channel
may travel not only downstream, but also upstream, what makes the numerical solution still expensive. As the flow rate in the channel increases (i.e., high Reynolds number but still laminar) the axial diffusive transport is diminished in comparison to the radial diffusion and the convective transport. Hence, only downstream processes matter, and all the second derivatives in axial direction can be eliminated in Eqs. (2, 4, 7) \cite{2, 108, 109}. Mathematically, the character of the equations is changed from elliptic to parabolic – a huge simplification, leading to much more efficient computational solution. This well-known simplification is generally known as the boundary-layer approximation, which is widely used in fluid mechanics. The boundary-layer equations form a system of differential-algebraic equations (DAE), with the time-like direction being the axial coordinate.

A further simplification for modeling channel flows consists in the assumption of infinite radial mass transport or at least very fast radial mass transport, leading to vanishing gradients of radial concentration and temperature. There is a large amount of literature discussing this so-called plug-flow (PF) model \cite{6}, which has been the model of choice until recently, including a variety of extensions such as mass transfer coefficients \cite{110} or two-phase approaches \cite{111}. The application of the PF model becomes unreliable for systems, in which fast catalytic reactions \cite{109} and/or homogeneous gas-phase reactions occur \cite{22}.

Further detailed simulations were for instance carried out by Hayes et al. \cite{112}, who developed a 2D finite-element model for the simulation of a single channel of honeycomb type monolith catalytic reactor; and Wanker et al. \cite{113} conducted transient two-dimensional simulations of a single channel of a catalytic combustor, taking into account the effects occurring in the gas phase, in the washcoat layer and in the substrate. They apply their model also to simulate a wood-fired domestic boiler \cite{114}.
6.6.6.2 Monolithic reactors

The simplest way to model honeycomb-like structures, as shown in Figure 1, is based on the assumptions that all channels behave essentially alike, and therefore only one channel needs to be analyzed. If upstream heat conduction does not matter, parabolic approaches as the boundary layer approximation may be used \(^{109}\), otherwise an elliptic ansatz is needed \(^{22,107}\). Heat transfer at the outer boundary of the monolith, spatially varying inlet conditions at the front face of the monolith, and different catalyst coatings will demand models that consider the entire monolithic structure. Since the detailed simulation of every individual channel is usually not tractable, simplifying algorithms are needed \(^{115}\). Catalytic monoliths for instance have been treated as porous media \(^{116}\), which can save computational time but could yield unreliable results if the interaction of transport and reactions in the individual channels matters.

Another approach combines the simulation of a representative number of channels with the simulation of the temperature profiles of the solid structure treating the latter one as continuum \(^{117-120}\). This approach is the basis for the computer code DETCHEM\textsuperscript{MONOLITH} \(^{91}\), which has been applied to model the transient behavior of catalytic monoliths. The code combines a transient three-dimensional simulation of a catalytic monolith with a 2D model of the single-channel flow field based on the boundary layer approximation. It uses detailed models for homogeneous gas-phase chemistry, heterogeneous surface chemistry, and contains a model for the description of pore diffusion in washcoats. The numerical procedure as sketched in Fig. 4 is based on the following ideas: The residence time of the reactive gas in the monolith channels is much smaller than the unsteadiness of the inlet conditions and the thermal response of the solid monolith structure. Under these assumptions, the time scales of the channel flow are decoupled from the temporal temperature variations of the solid, and the following procedure can be applied: A transient multi-dimensional heat balance is solved for the monolithic structure including the thermal insulation and reactor walls, which are treated
as porous continuum. This simulation of the heat balance provides the temperature profiles along the channel walls. At each time step the reactive flow through a representative number of single channels is simulated including detailed transport and chemistry models. These single-channel simulations also calculate the heat flux from the fluid flow to the channel wall due to convective and conductive heat transport in the gaseous flow and heat released by chemical reactions. Thus, at each time step, the single-channel simulations provide the source terms for the heat balance of the monolith structure while the simulation of the heat balance provides the boundary condition (wall temperature) for the single-channel simulations. At each time step, the inlet conditions may vary. This very efficient iterative procedure enables a transient simulation of the entire monolith without sacrificing the details of the transport and chemistry models, as long as the prerequisites for the time scales remain valid. Furthermore, reactors with alternating channel properties such as flow directions, catalyst materials, and loadings can be treated. The code has been applied to model transient behavior of automotive catalytic converters, catalytic combustion monoliths for gas-turbine applications, and high temperature catalysis. Exemplarily, Figure 5 reveals the time-resolved temperature and species profiles in a single channel of a catalytic monolith for partial oxidation of methane and the temperature distribution of the solid structure during light-off\textsuperscript{[55]}. 

6.6.6.3 Fixed bed reactors

The understanding of fluid dynamics and their impact on conversion and selectivity in fixed bed reactors is still very challenging \textsuperscript{[121, 122]}. For large ratios of reactor width to pellet diameter, simple porous media models as discussed in Section 6.6.4.1 are usually applicable \textsuperscript{[123]}. This simple approach becomes questionable as this ratio decreases \textsuperscript{[76, 124]}. At small ratios the individual local arrangement of the particles and the corresponding flow field are significant for mass and heat transfer, and, hence, the overall product yields. Therefore, several attempts have recently been made to resolve the flow field in the actual configuration.
Meanwhile it is possible to simulate complex geometries of packings without simplifications \cite{67, 125-130}. Even though the governing equations are relatively simple for laminar flows (Section 6.6.1), this approach can only be applied for small and periodic regions of the reactor due to the huge number of computational cells.

Nijemeisland and Dixon\cite{131} conducted a CFD simulation of the turbulent flow and heat transport in a periodic test cell with a tube-to-particle diameter ratio of 4; the geometry is shown in Figure 6. The turbulence was modeled by the Renormalization Group (RNG) $k$-$\varepsilon$ model \cite{132}, and two different wall functions (standard \cite{133} and non-equilibrium) were applied to model the flow field near solid surfaces. The resulting temperature profile is shown in Figure 6. Attempts to correlate the local wall heat flux with local properties of the flow field, such as velocity components, velocity gradients, and components of vorticity, led to the conclusion that local heat transfer rates do not correlate statistically with the local flow field. Instead, a conceptual analysis was used to suggest that local patterns of wall heat flux are related to larger-scale flow structures in the bed.

Recently, Lattice-Boltzmann-methods (LBM) have been applied for a better understanding of fluid flow in complex reactor configurations \cite{87, 88, 134}. The packing of spheres in cylindrical columns can be created either from experimental observations, such as magnetic resonance imaging (MRI), or by computer simulations. The created topology is then divided into a Cartesian grid, where individual elements are labeled as solid or fluid regions. A high resolution of the grid leads to accurate flow profiles. Zeiser et al.\cite{88} generated the geometrical structures of the fixed bed with a Monte-Carlo method. This allowed to simulate efficiently the placement of randomly packed spheres in a cylinder and to obtain detailed information of statistical properties, such as the distribution of the void fraction. This geometrical information was the basis for subsequent numerical flow simulation using LBM. This approach allowed the prediction of the local fluid velocity distribution in the bed as well as the transport and rate of simple chemical reactions. Yuen et al.\cite{134} studied correlations
between local conversion and hydrodynamics in a 3D fixed-bed esterification process by applying a LBM and comparing its results with data from in situ magnetic resonance visualization techniques.

6.6.6.4 Wire gauzes

Wire gauze reactors have been applied for high temperature catalytic reactions in industry for quite a long time. For example, ammonia is oxidized over Pt/Rh wire gauzes to produce NO (Ostwald process), and similar, HCN is synthesized by ammoxidation of methane (Andrussov process).

Due to the complex 3D geometry, wire gauze reactors have been frequently treated by simpler two dimensional simulations [135, 136]. However, since mass and sometimes heat transport are the dominating processes in wire gauze reactors, simplifications of the flow field are risky. Recently, first CFD studies were performed using 3D simulations of the flow field. The 3D flow field through knitted gauzes applied for ammonia oxidation was recently simulated by Neumann et al. [137]. Figure 7 reveals the predicted temperature distribution in the catalyst gauze.

Catalytic partial oxidation (CPOX) of light alkanes was also studied in wire gauze reactors. De Smet et al. [138] studied CPOX of methane with oxygen at atmospheric pressure in a continuous-flow reactor containing a single Pt metal gauze. They used 3D computations of simultaneous heat and mass transfer in case of a simple surface reaction on the gauze catalyst to derive intrinsic kinetics. Recently, a 3D CFD simulation of their experiment was conducted that even included detailed surface and gas phase reaction schemes [139].

6.6.6.5 Catalytic reactors with multi-phase fluids

CFD simulations have recently been applied to quite a number of catalytic reactor types with multi-phase flow fields such as fluidized bed reactors with and without circulation, slurry
reactors, trickle-bed reactors, membrane reactors, electro-catalytic devices (e.g. fuel cells), and reactive distillation devices. These multi-phase reactors are of multi-scale structure, i.e. single particles, particle clusters/bubbles and reactor vessel, and of multiple physics, i.e. hydrodynamics, heat and mass transfer, and reaction kinetics. The formation of complex structures/patterns in each regime is a result of a compromise between dominant mechanisms at multiple scales. Coupling of hydrodynamics, heat and mass transfer, and reaction kinetics takes place at molecular and particle levels where conductive and convective transfer and diffusion within the internal pores of the catalyst are accompanied by the adsorption, surface reaction and desorption of reactant and product on the surface. Even though this complexity is challenging for CFD simulations, computations are a promising tool to achieve a better understanding of multi-phase reactors.

A detailed description of the fundamentals and modeling attempts of these multi-phase reactors is beyond the scope of this Chapter. Instead, an example may serve as illustration of the potential of CFD simulations of reactors with multi-phase flow fields: The CFD code FLUENT was applied to study the catalytic decomposition of ozone ($O_3$) by sand particles impregnated with iron oxide in a fluidized bed, where ozone enters the bed in a uniform flow from the bottom \[92\]. As it passes through the bed, $O_3$ interacts with the catalyst and is converted to molecular oxygen. Figure 8 shows the gas volume fraction in the bed after one second of operation (red corresponding to 100% gas). It is observed that small bubbles gather together into larger bubbles and create a desired hydrodynamic state for optimum conversion.

CFD simulations have recently been applied to far more catalytically reactive systems than described so far. Here, only references to some of the literature can be given: poly electrolyte membrane (PEM) \[140, 141\] and solid oxide (SOFC) \[142, 143\] fuel cells, fibrous active materials \[144, 145\], gas-liquid-solid reactors \[146\], monolithic loop-reactors \[147\].
6.6.7 Summary and outlook

From a reaction engineering perspective, computational fluid dynamics simulations have been matured to a powerful tool for understanding mass and heat transport in catalytic reactors. Initially, CFD calculations focused on a better understanding of mixing, mass transfer to enhance reaction rates, diffusion in porous media and heat transfer. Over the last ten years, the flow field and heat transport models have also been coupled with models for heterogeneous chemical reactions. So far, most of these models are based on the mean field approximation, in which the local state of the surface is described by its coverage with adsorbed species averaged on a microscopic scale. The currently increasing research activities on surface reactions at practical conditions will certainly boost the application of CFD codes that combine fluid flow and chemistry. New insights into the complexity of heterogeneous catalysis, however, will also reveal the demand for more sophisticated chemistry models. Their implementation into CFD simulations will then even require more sophisticated numerical algorithms and computer hardware. Hence, CFD simulations of reactive systems will remain a very active field and the implementation of more adequate and complex models will continue.

The simulation results will always remain a reflection of the models and physical parameters applied. The careful choice of the sub models (geometry, turbulence, diffusion, species, and reactions involved, etc.) and the physical parameters (inlet and boundary conditions, conductivity, permeability, viscosity, etc.) is a precondition for reliable simulation results. Therefore, only the use of appropriate models and parameters, which describe all significant processes in the reactor, can lead to reliable results. Furthermore, numerical algorithms never give the accurate solution of the model equations but only an approximated solution. Hence, error estimation is needed. Having these crucial issues in mind, CFD can really serve as powerful tool in understanding the behavior in catalytic reactors and in supporting the design and optimization of reactors and processes.
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6.6.8 References


FIGURES

Figure 1: Catalytic combustion monolith and physical and chemical process occurring in the single monolith channel.

Figure 2: Survey of the methodology of the development of a surface reaction mechanism.
Figure 3: LIF measurements (a) and predictions (b-d) of OH radical profiles in the transition from heterogeneous to homogeneous oxidation of methane in a Pt coated channel at 6 bar; three different wide-spread reaction schemes were evaluated revealing the reliability of scheme (b) and deficiencies of the schemes (c) and (d). The Figures were taken from Reinke et al. \cite{69}.

Figure 4: Structure of the computer code DETCHEM\textsuperscript{MONOLITH} \cite{91}.
Figure 5: Simulation of light-off of a monolithic reactor coated with Rh for partial oxidation of methane to synthesis gas \cite{55}. Temperature of the solid structure (top) and gas-phase temperature and species mole fractions in a single channel in the center of the monolith (below), red = maximum, blue = minimum.
Figure 6: Computational grid structure and computed temperature profile in a vertical plane of a CFD simulation of a fixed bed reactor, taken from Nijemeisland and Dixon \cite{131}.

Figure 7: Computed temperature profile in a MULTINIT\textsuperscript{®} catalyst gauze (flow direction from left to right), taken from Neumann et al. \cite{137}.
Figure 8: Computed gas volume fraction in the fluidized bed after 1 second of operation (red corresponding to 100% gas), taken from [92] (Example X241).