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Detailed numerical simulations of catalytic fixed-bed reactors: Heterogeneous dry reforming of methane



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HIGHLIGHTS

- Fully 3D CFD modeling of randomly packed catalytic fixed-bed reactor.
- CFD model combines complex geometry with detailed kinetics of DRM.
- Meshing recommendations are given due to grid sensitivity studies.
- Determination of regions with catalyst deactivation by surface-adsorbed carbon.

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ABSTRACT

Highly endothermic (or exothermic) heterogeneous catalytic reactions are performed commonly in fixed-bed reactors with small tube-to-particle-diameter ratios N both in industrial and lab-scale applications. For these reactor configurations conventional plug flow models and pseudo-homogeneous kinetic models fail. An adequate modeling can be carried out with full computational fluid dynamics (CFD) in combination with detailed reaction mechanisms. In this study, a full three-dimensional fixed-bed reactor for the catalytic dry reforming of methane (DRM) over rhodium was simulated with a detailed reaction mechanism. The bed consists of 113 spherical solid particles in which thermal conductivity was considered. Two different Reynolds numbers were investigated, i.e., 35 and 700. The simulated DRM fixed-bed reactor demonstrates the strong interaction between chemical kinetics and transport of momentum, heat and mass. The observed velocity, temperature and species fields are characterized by their three-dimensional behavior and interactions highlighting their complexity and discrepancy from lumped model predictions. In addition, the reaction mechanism determines regions with catalyst deactivation by carbon deposition. This study demonstrates the advantages of modeling heterogeneous catalytic fixed-bed reactors with small N fully in three-dimensional in combination with detailed reaction mechanisms. Finally, this modeling approach reduces dependencies on empiricism for the calculation of multiscale reaction devices.

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1. Introduction

The atmospheric concentration of “greenhouse” gases, i.e., carbon dioxide (CO₂), nitrous oxide (NO), methane (CH₄) and chlorofluorocarbons (CFCs), has increased dramatically during the last decades (Hartmann et al., 2013). These anthropogenic emissions have risen a global concern over the current technological practices. Hence, the field of interest involves CH₄ and CO₂ disposal, utilization and removal, as well as the effect of these gases in the atmosphere (Mikkelsen et al., 2010; Centi and Perathoner, 2009; Hunt et al., 2010; Papadopoulou et al., 2012;

Balat and Öz, 2007). However, the general engineering interest lies in processes in which CH₄ and CO₂ react to synthesis gas or syngas, i.e., CO+H₂. On one hand syngas can be used to produce liquid fuels via the Fischer–Tropsch reaction; a review given in Dry (2002). On the other hand syngas can be utilized in chemical energy transmission systems (Wang et al., 1996).

Dry reforming of methane (DRM) is such a process in which CH₄ and CO₂ react to syngas:



This highly endothermic process is performed at temperatures of 700–1000 °C. One of the largest obstacles for the industrial use of DRM is coke formation, which quickly leads to a deactivation of the catalyst (Chen et al., 2001; Ginsburg et al., 2005; Guo et al., 2007).

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This prospective process has to be carried out with an appropriate catalyst. In the last decades Nickel-based catalysts and noble metal-supported catalysts (Rh, Ru, Pd, Pt, Ir) have shown encouraging performances regarding conversion and selectivity (Tornaiainen et al., 1994; Wang et al., 1996; Guo et al., 2004). Rhodium for example is characterized by its low affinity for carbon formation and its high activity (Rostrup-Nielsen and Hansen, 1993; Bradford and Vannice, 1999).

Typical reactor types for endothermic (or exothermic) reactions are fixed beds, foams, multi-channel reactors or fluidized-bed reactors. Still today, the most common way to carry out a heterogeneous catalytic reaction is a fixed-bed reactor. Randomly distributed catalytic particles are the simplest type of such a reactor, whereas particle diameters range from 2 to 10 mm (Eigenberger, 2008). For the DRM the heat transfer inside the reactor is one of the major engineering issues. Thus, small reactor tubes are desirable. Additionally, high gas velocities and reasonable pressure drops constrain the particle diameter to be quite large. Hence, fixed beds with a small tube-to-particle-diameter ratio ($4 < N < 15$) are preferable. In some lab-scale applications even $N < 4$ were carried out, e.g., Leva et al. (1951), Reichelt (1972), Vortmeyer and Winter (1984), and Dixon (1997). In all cases, randomly packed beds are characterized by inhomogeneous structures. Especially for small N the inhomogeneities become dominant resulting in significant wall effects, local back flows and large axial as well as radial gradients. Consequently, conventional descriptions, based on plug flow and pseudo-homogeneous kinetics, are questionable for these fixed-bed configurations (Bey and Eigenberger, 1997; Dixon, 1997; Bauer and Adler, 2003; Freund et al., 2005; Gräf et al., 2014). The strong interplay between velocity, temperature and species distribution makes the fixed-bed reactor a very interesting and likewise challenging device for chemical engineers. It includes several time and length scales. The multiscale modeling, or first-principles approach (Dudukovic, 2009), pursues to describe entirely the system by theory of the actual phenomena, i.e., elementary reaction steps at the catalyst surface and a detailed characterization of the fluid flow. As a consequence, an adequate description of catalytic fixed-beds should include the rigorous modeling with full computational fluid dynamics (CFD) in the interstitial regions as well as in the solid in combination with detailed chemical reaction models (also called the micro-kinetics).

In recent years, several authors have simulated spatially resolved fixed-bed reactors accounting for radial, axial and circumferential profiles (Dixon and Nijemeisland, 2001; Guardo et al., 2005; Ookawara et al., 2007; Bai et al., 2009; Eppinger et al., 2011; Behnam et al., 2013). However, only few have coupled the fluid dynamics of fixed-beds with catalytic reactions (Kuroki et al., 2009; Taskin et al., 2010; Dixon et al., 2012). That means the already complex equation system will be extended by species conservation equations. Several authors used pseudo-homogeneous kinetics in combination with detailed fluid dynamics, due to the small number of reaction equations. However, these kinetics are often limited to a certain range of process parameters and could therefore not be applied to other flow regimes or reactor types (Saliccioli et al., 2011). Especially the species development inside fixed-bed reactors are often insufficient reproduced with such kinetics in contrast to the exit concentrations, which was recently demonstrated by Korup et al. (2011). As Wehinger et al. (2014) concluded spatially resolved fluid dynamics must be combined with reliable kinetics, i.e., detailed reaction mechanisms. Several detailed methane reforming kinetics over rhodium were published validated over an operating range relevant to industrial applications and claimed to be thermodynamically consistent (Hickman and Schmidt, 1993; Mhadeshwar and Vlachos, 2005; Maestri et al., 2008, 2009; McGuire et al., 2011; Kahle et al., 2013). Finally, the combination of a first-principle approach at different scales, i.e., detailed reaction mechanism at the

catalyst scale and full Navier–Stokes equations at the reactor scale, helps to obtain a fundamental understanding of chemical reactors.

In this study, we investigated spatially resolved heterogeneous catalysis of the dry reforming of methane over rhodium in a fixed-bed reactor in terms of combining full CFD simulations with a detailed reaction mechanism from McGuire et al. (2011). A catalytic fixed-bed reactor with spherical solid particles and a small tube-to-particle-diameter ratio ($N=4$) was numerically simulated. The aim of the study was firstly to obtain a better understanding of the strong interactions between catalytic reactions and the surrounding flow in fixed-bed reactors. Secondly, we investigated the feasibility to model catalytic fixed-bed reactors in an adequate multiscale way.

2. Simulating heterogeneous fixed-bed reactors

2.1. Modeling chemically reactive flow

2.1.1. Governing equations

For the simulations in this study, full three-dimensional governing equations were applied. The conservation of total mass, momentum in x -, y -, z -directions, mass of species and energy leads to the solution for velocity, pressure, temperature and species concentration in the calculation domain. A laminar problem with Einstein convention can be written as follows.

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_i)}{\partial x_i} = 0 \quad (2)$$

where ρ is the mass density, t is the time, x_i are the Cartesian coordinates and v_i are the velocity components.

Conservation of momentum:

$$\frac{\partial(\rho v_i)}{\partial t} + \frac{\partial(\rho v_i v_j)}{\partial x_j} + \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} = \rho g_i \quad (3)$$

The stress tensor τ_{ij} is written as follows:

$$\tau_{ij} = -\mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) + \left(\frac{2}{3} \mu \right) \delta_{ij} \frac{\partial v_k}{\partial x_k} \quad (4)$$

where μ is the mixture viscosity and δ_{ij} is the Kronecker delta, which is unity for $i=j$, else zero.

Conservation of species i :

$$\frac{\partial(\rho Y_i)}{\partial t} + \frac{\partial(\rho v_j Y_i)}{\partial x_j} + \frac{\partial(j_{i,j})}{\partial x_j} = 0 \quad \text{for } i = 1, \dots, N_g \quad (5)$$

with mass fraction $Y_i = m_i/m$ of species i and total mass m . N_g is the number of gas phase species. The components $j_{i,j}$ of the diffusion mass flux are described by the mixture-average formulation:

$$j_{i,j} = -\rho \frac{Y_i}{X_i} D_i^M \frac{\partial X_i}{\partial x_j} - \frac{D_i^T}{T} \frac{\partial T}{\partial x_j} \quad (6)$$

where D_i^M is the effective diffusivity between species i and the remaining mixture. X_i represents the molar fraction of species i . M_i is the molecular weight of species i and T is the temperature. The binary diffusion coefficients D_i are obtained through polynomial fits. The molar fraction X_i can be written as

$$X_i = \frac{1}{\sum_{j=1}^{N_g} \frac{Y_j}{M_j}} \frac{Y_i}{M_i} \quad (7)$$

Conservation of energy in terms of specific enthalpy h is as follows:

$$\frac{\partial(\rho h)}{\partial t} + \frac{\partial(\rho v_j h)}{\partial x_j} + \frac{\partial(j_{q,j})}{\partial x_j} = \frac{\partial p}{\partial t} + v_j \frac{\partial p}{\partial x_j} - \tau_{jk} \frac{\partial v_k}{\partial x_k} + S_h \quad (8)$$

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