Chemical Engineering Science 111 (2014) 220–230

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Fluidic effects on kinetic parameter estimation in lab-scale catalysis testing – A critical evaluation based on computational fluid dynamics

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HIGHLIGHTS

- Two different lab-scale catalytic reactors were simulated.
- Fluidic effects on kinetic parameter estimation were specified.
- Stagnation flow reactors are suitable to suppress fluidic effects.
- Neglecting radial profiles leads to erroneous kinetic parameters for fixed-beds.
- The prediction of temperature profiles is of major importance.

ARTICLE INFO

Article history:
Received 18 December 2013
Received in revised form
10 February 2014
Accepted 17 February 2014
Available online 6 March 2014

Keywords:
Catalysis
Chemical reactors
Computational fluid dynamics
Kinetics
Oxidative coupling of methane
Dry reforming of methane

ABSTRACT

The influence of fluidic effects on two different kinetic parameter identifications in lab-scale catalysis testing was investigated using computational fluid dynamics. Firstly, the dry reforming of methane in a stagnation flow reactor with a detailed surface mechanism was simulated fully in three-dimensional. It is shown that the 3D simulations are not advantageous over the commonly used stagnation-flow boundary-layer problem description. This reactor setting is a valuable example of how fluidic effects on kinetic parameter estimation can be suppressed. Secondly, the oxidative coupling of methane in a fixed-bed reactor with a 10-step kinetic mechanism was simulated with a porous-media model. The experimental results could not be reproduced. The underlying plug-flow model for kinetic parameter identification fails in this highly exothermic reactor, because of significant radial temperature profiles and resulting radial concentration profiles. The correct prediction of temperature profiles is of major significance. This investigation highlights the importance of well defined reactor configurations in combination with spatially resolved temperature and concentration profiles for the determination of reliable kinetic parameters for highly exothermic or endothermic reactions.

1. Introduction

Over the last decades the utilization of computers in the field of chemical reactor description and design has increased dramatically. This is not only due to faster and cheaper technical devices but also due to the usability of CFD-codes either commercial or non-commercial. One of the preconditions in reactor modeling is the knowledge of the reaction kinetics. Especially when catalysts are involved in chemical reactions, i.e., in more than 80–90% of industrial processes today (Marcilly, 2003), kinetic description can be critical. Many of the kinetics used for reactor design are Langmuir–Hinshelwood–Hougen–Watson (LHHW) types. However, parameters of these models can be questionable and the fundamental mechanisms elusive, although the specific LHHW model is capable to reproduce experiments accurately, cf. Salciccioli et al. (2011). Consequently, a reactor scale-up with such a model would lead to erroneous predictions.

In all chemical reactors, there is an interplay between chemical kinetics and transport of momentum, heat and mass. Different time and length scales appear at different facets of a reactor process. The so-called multiscale methodology gives a quantitative correlation between various measures of performance and operating variables (Dudukovic, 2009). At different levels of knowledge descriptions can be carried out. At the reactor scale, the depth ranges from ideal reactors to computational fluid dynamics (CFD) (Dudukovic, 2010).

Not only in extremely exothermic and endothermic reactions, the chemistry and transport phenomena are intrinsically connected. However, in those reactions it is more complicated to distinguish between the different contributions. Dautzenberg and

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http://dx.doi.org/10.1016/j.ces.2014.02.025

colleagues have highlighted how to minimize the effects of transport phenomena while estimating kinetic parameters in their “Ten Commandments for Testing Catalysts” (Dautzenberg, 1989). Nevertheless, the impact of fluidic effects in the reactor toward the estimated kinetics is often not further specified. Simplified chemical models fail when chemical coupling with gas phase reactions is important or where a large proportion of the heat-release occurs in the boundary-layer (Pfefferle, 1995). Plug flow reactor models, for example, are unsatisfactory for catalytic combustion applications, because they simplify drastically the heat and mass transport (Dalle Nogare et al., 2008). It is therefore recommended to model such reactors with full CFD or at least lumped fluid dynamic models, e.g., pseudo-heterogeneous models (Korup et al., 2013). Several authors have highlighted the importance to determine mass transport limitations while measuring catalytic reactions (Horn et al., 2007; Kapteijn and Moulijn, 2008; Schuurman, 2008).

One of the critical points in the identification of kinetic parameters is the temperature profile. It is influenced by and likewise influences the reaction path. However, the modeling is complex, since temperature is influenced by several physical transport processes, e.g., heat released by reaction can be transferred by conduction and convection through the fluid, conduction through the particles and radiation (Wolf et al., 1997; Dixon, 2012). It was shown that the kinetics will be more influenced by the temperature profile than vice versa (Dalle Nogare et al., 2011). In other words a model that is capable to predict the temperature profiles is able to predict the species profiles correctly.

Being aware of these considerations, several scientists investigated spatially resolved experimental data in combination with spatially resolved numerical data, in recent years. Other authors have emphasized the testing under realistic conditions besides spatially resolution (Horn et al., 2006; Urakawa and Baiker, 2009; Korup et al., 2013). Some of these configurations are: 3D simulated catalytic gauze, e.g., Rinnemo et al. (1997) and Quiceno et al. (2006), 1D simulated catalytic foam, e.g., Horn et al. (2007), Dalle Nogare et al. (2011) and Korup et al. (2013), 3D simulated channel with catalytic walls, e.g., Sa et al. (2010) and Hettel et al. (2013), 1D or 2D simulations of stagnation flow reactors, e.g., McGuire et al. (2009, 2011), Karakaya and Deutschmann (2013) and Yuan et al. (2008), and 1D simulated annular reactors, e.g., Maestri et al. (2008).

In this paper, we investigated two current catalytic reactions, i.e., the dry reforming of methane (DRM), an overview given by Bradford and Vannice (1999), and the oxidative coupling of methane (OCM), a review is presented by Arndt et al. (2011). The focus lies on two kinetic descriptions: a detailed surface mechanism for DRM, cf. McGuire et al. (2011), and a homogeneous-heterogeneous OCM-kinetics by Stansch et al. (1997). The reactor configurations of each experiment were reproduced by 3D chemically reacting flow simulations. The results of the experiments and simulations are presented, compared and discussed with special attention to the temperature contribution. The influences of the chosen reactor type toward fluid dynamics and therefore kinetic parameter estimation were investigated.

2. Simulating chemically reacting flow

In this study, full three-dimensional governing equations form the basis for the calculations. They represent the most precise description of reacting flow in an arbitrary geometry (Mladenov et al., 2010). The conservation of total mass, momentum in x, y, z directions, mass of species and energy provides the solution for velocity, pressure, temperature and species concentration in the calculation domain. The equations for a laminar problem are with Einstein convention.

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_i)}{\partial x_i} = 0 \tag{1}$$

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:

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

The stress tensor τ_{ij} is given by

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

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:

$$\frac{\partial(\rho Y_i)}{\partial t} + \frac{\partial(\rho v_j Y_i)}{\partial x_j} + \frac{\partial(j_{i,j})}{\partial x_j} = R_i^{hom} \quad \text{for } i = 1, \ldots, N_g \tag{4}$$

with Y_i the mass fraction of species i in the mixture $Y_i = m_i/m$ with m as total mass. R_i^{hom} is the net production rate by homogeneous reactions, whereas N_g represents the number of gas phase species. The components $j_{i,j}$ of the diffusion mass flux are modeled by the mixture-average formulation:

$$j_{i,j} = -\rho\frac{Y_i}{X_i}D_i^M\frac{\partial X_i}{\partial x_j} - \frac{D_i^T}{T}\frac{\partial T}{\partial x_j} \tag{5}$$

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

$$X_i = \frac{1}{\sum_{j=1}^{N_g}\frac{Y_j}{M_j}}\frac{Y_i}{M_i} \tag{6}$$

Conservation of energy in terms of specific enthalpy h:

$$\frac{\partial(\rho h)}{\partial t} + \frac{\partial(\rho v_j h)}{\partial x_j} + \frac{\partial j_{q,j}}{\partial x_j} = \frac{\partial p}{\partial t} + v_j\frac{\partial p}{\partial x_j} - \tau_{jk}\frac{\partial v_j}{\partial x_k} + S_h \tag{7}$$

where S_h is the heat source. Diffusive heat transport $j_{q,j}$ is defined as

$$j_{q,j} = -\lambda\frac{\partial T}{\partial x_j} + \sum_{i=1}^{N_g} h_i j_{i,j} \tag{8}$$

with thermal conductivity of the mixture λ and mixture specific enthalpy h:

$$h = \sum_{i=1}^{N_g} Y_i h_i(T) \tag{9}$$

with the specific enthalpy as a function of temperature $h_i = h_i(T)$.

Ideal gas was assumed connecting pressure, temperature and density to close the governing equations:

$$p = \frac{\rho R T}{\sum_{i=1}^{N_g} X_i M_i} \tag{10}$$

In addition, NASA polynomial functions were used to derive heat capacity $c_{p,i}$. For more information see Deutschmann (2008) and Kee et al. (2003).

All simulations were carried out with the simulation software STAR-CCM+ version 8.04.010 of CD-adapco (2013).