RESOLVED-PARTICLE FIXED BED CFD WITH MICROKINETICS AND ANISOTROPIC DIFFUSION

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Abstract

Microkinetics models for the partial oxidations of ethylene and of methanol on silver catalysts are coupled with computational fluid dynamics and implemented in a randomly packed bed of 120 spherical particles. The model includes interactions of the elementary reaction steps and transport inside the particles and the flow field. The effects of using the full implementation of the microkinetics and a flux dependent anisotropic diffusivity on the model are presented and compared to simplified approaches.

Keywords

Computational Fluid Dynamics, Microkinetics, Fixed bed

Introduction

Partial oxidation reactions are highly exothermic, and carbon dioxide is the major by-product. An increase in selectivity reduces carbon emissions and improves the efficiency of the plant. Molecular level studies in recent years have provided us an in-depth understanding of the reaction mechanisms on the surface of the catalyst. However, due to the fast and exothermic nature of these reactions, extreme temperature and species gradients form in an industrial scale reactor which molecular level studies alone cannot address. Therefore, integrating detailed kinetics and transport inside the solid with the fluid phase is necessary to achieve a comprehensive model (Figure 1).

To date, several efforts have been made to couple full microkinetics with CFD in fixed bed reactors, however, they either neglected the reaction inside the solid particles (Wehinger et al., 2015) or did not study the reaction under the steady state conditions (Maffei et al., 2016). Here we propose an efficient method for implementing microkinetics models in our CFD model under steady state conditions for multiple reactions, and compare the results with methods in which simplified microkinetics are used.

Methods

A randomly packed bed of 120 spheres is used for the geometry of the model. The “bridges” approach is used to handle the contact points between the particles, and effective heat conductivity is defined for modeling heat transfer between the tube wall and the particles.

At the catalyst pore-scale, a flux-dependent anisotropic diffusivity is implemented into the model to address the effects of the species flux on the diffusion coefficients in the mixture. Hite and Jackson’s (1977) derivation of the Dusty Gas Model is used without assuming that the ratio of the fluxes is constant.

Two different methods are used to incorporate microkinetics into CFD. Initially, reduced microkinetics models are developed based on Campbell’s degree of rate control and hybrid steady state assumption. As a result, explicit rate expressions are derived based on species partial pressures and kinetic parameters, and implemented

Figure 1. (a) Streamlines, (b) mass fraction of EO on the surface of the particles, and (c) EO surface sites inside the catalyst particles, in a randomly packed bed of 120 spherical particles.
as source terms in the solid particle model (Dixon et al., 2010).

The second approach is implementation of the full microkinetics using tabulated Turnover frequency (TOF) data. In this approach microkinetics models are solved for the steady state conditions for a wide range of different temperatures and species concentrations. Then TOF data are mapped into quadratic multivariate splines which later are used in CFD simulations for evaluation of the rates of the elementary steps and the surface sites in the solid particles. The splines evaluate reaction rates with relative error of less than 0.008. Therefore, the method evaluates reaction rates with high accuracy without slowing down the simulations.

Surface sites of the species and intermediates are affected by the reactor conditions, and they can be studied to address important issues such as site blocking of non-reacting intermediates, and product inhibition under industrial conditions.

![Figure 3. EO rate variation with angular coordinate θ on a horizontal plane through the center of particle at r = R/2 for different diffusion models.](image)

**Conclusions**

A method has been developed to couple CFD with full microkinetics models and improved pellet diffusion models under steady state conditions. Results have been compared with simulations based on simplified microkinetics. The method enables us to monitor important catalyst features under reaction conditions; therefore, it can be used to

1. Study computationally designed catalysts and kinetic models under realistic reaction conditions.

2. Study the existing systems in detail, and then simplify them to practical 2D reaction engineering models.

**References**


**Results**

Different case studies are carried out to study the implementation of simplified and full microkinetics in CFD simulations, and effects of the flux dependent diffusivity on them. It is observed that for ethylene oxide the reduced microkinetics model causes deviation of the species and temperature gradients from the full model in CFD simulations (Figure 2). This is in agreement with the literature (Stegelmann et al., 2004). Due to the complexity of the mechanism general rate expressions are only valid under certain operating conditions. It can be shown that the rate determining-steps are changing in different regions of the reactor, and from the surface to inside of the solid particles. However, this inconsistency between the two models is not significant in the methanol oxidation case. This is due to the simplicity of the microkinetics model (Andreasen et al., 2003).

Figure 3 shows the effects of the isotropic, and the flux dependent anisotropic effective diffusivities on the reaction rate inside a particle in the reactor. The anisotropic model accounts for mass transfer limitation inside the particles due to species flux changes.

![Figure 2. Temperature (K) contours on a mid-plane through the bed for (a) simplified microkinetics and (b) full microkinetics in ethylene oxidation reactor.](image)