A multi-region model for reaction–diffusion process within a porous catalyst pellet

Hua Li, Mao Ye *, Zhongmin Liu

Dalian National Laboratory for Clean Energy, National Engineering Laboratory for MTO, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

HIGHLIGHTS

- A meso-scale multi-region model is developed for a single porous catalyst pellet.
- The numerical methods are proposed for multi-scale reaction–diffusion problems.
- The model is validated against the alkylation of benzene over H-ZSM-5 crystal particles.
- The effects of volume fraction, size, and spatial distribution of H-ZSM-5 crystal particles are studied.

ARTICLE INFO

ABSTRACT

In this paper, a multi-region model based on the unified Maxwell–Stefan diffusion theory is developed to investigate the reaction–diffusion processes within catalyst pellets formed by micro-pore particles and meso/macro-pore support. The corresponding partial differential equation (PDE) systems, describing chemical reactions, bulk diffusion, Knudsen diffusion, surface diffusion and viscous flow, are converted to ODE systems based on finite volume method (FVM). The resulting multi-scale ODE systems are solved by reduced storage matrix method, where a quasi-stationary state assumption is adopted in the numerical solution to solve multi-scale problem in which the diffusivities of micro-pores and meso/macro-pores are significantly different. The alkylation of benzene over a single multi-porous pellet formed with H-ZSM-5 crystal particles was simulated as an example. The effects of volume fraction, size and spatial distribution of H-ZSM-5 crystal particles on the effectiveness factor of the catalyst pellet were then investigated and discussed. It is shown that the multi-region model is a potential bottom to up tool for reaction–diffusion processes in catalyst pellet exhibiting multi-scale time characteristic.

1. Introduction

Zeolite catalysts see their applications in a variety of industrial sectors including, among others, fluid catalytic cracking (FCC) and methanol to olefins (MTO). Despite the complex mass and heat transfer between catalyst pellets and surrounding fluid, the performance of single catalyst pellet affects the reactor operation significantly. The latter is strongly dependent upon the transport phenomena inside the catalyst pellet, such as reactants adsorption, multi-component diffusion, surface reaction, and reactants and products desorption (Keil, 2012, 2013). Practically zeolite catalyst pellets used in industrial reactors have complicated porous structures, in which pores with different sizes may co-exist. For instance, an industrial MTO

catalyst pellet is composed of micro-pore SAPO-34 zeolite crystal particles and macro/meso-pore catalyst support (or called matrix). Here the micro-pores refer to the pores smaller than 2 nm, the macro-pores refer to those larger than 50 nm, and the meso-pores are in between (Krishna, 1993; Krishna and Wesselingh, 1997). The same can be found in industrial FCC catalyst pellet where the micro-pore Y zeolite crystal particles are surrounded by macro/meso-pore catalyst support. The study of reaction and molecular diffusion in the micro-pore zeolite crystals has received considerable interest in past decades (Kärger and Ruthven, 1992; Chen et al., 1994). However, despite the diffusion-reaction process inside the zeolite crystals, the transport and thus the reaction in an industrial zeolite catalyst pellet are also highly related to the number, position, and size distribution of the micro-pore zeolite crystal particles. Previous studies found that the effectiveness factor of a single micro-pore crystal particle decreases as the particle size increases due to the diffusion limitations (Hansen et al., 2009).

As the diffusion coefficients (the bulk diffusion combined with Knudsen diffusion) in the macro/meso-pores may be 4–6 orders of magnitude higher than that of surface diffusion in the micro-pores, it is usually assumed that the macro/meso-pores do not significantly affect intracrystalline diffusion, and only a few studies concerning the transport of reactants and products in macro/meso-pores in the catalyst support have been reported so far in the open literature (Hinderer and Keil, 1995; Keil et al., 1999). A series of experimental studies by Kortunov et al., (2005) showed that the diffusion in macro/meso-pores in fact plays an important role in the transport inside catalyst pellets. In this connection, in order to improve the diffusivity of reactants and products and thus enhance the reaction rates in the catalyst pellet, the number, position, and size distribution of micro-pore crystal l particles have to be optimized by considering the diffusion in both macro/meso-pores and micro-pores simultaneously. Currently researchers and engineers mainly use the trial and error method to optimize the catalyst based on the conversion and selectivity data obtained in the laboratory scale experiments, which certainly elaborates the process of catalyst development. Apparently the understanding of the transport and thus reaction in real industrial catalyst pellet still requires significant effort. As the first step toward this ambition, the aim of this paper is to develop a modeling approach in which the diffusion in both micro-pores and macro/meso-pores can be studied simultaneously.

Obviously, the modeling approach capable of addressing the diffusion-reaction process in both micro-pores and macro/meso-pores simultaneously has to deal with different diffusion mechanisms dwelled in different pore sizes. From the view of modeling hierarchy, this model could be regarded as a meso-scale model (medium level). In the literature, though a variety of modeling approaches have been developed for the diffusion-reaction process in a catalyst pellet, there are few meso-scale models for catalyst pellets (Hansen et al., 2009; Solsvik and Jakobsen, 2012). Most models could be ascribed to micro-scale and macro-scale models. Micro-scale models are at the lowest level for catalyst particles, their research objects focus only on zeolite crystals. Keil (2012) and Hansen and Keil (2012) recently proposed a hierarchical modeling strategy for diffusion-reaction process in zeolite crystals, in which the first principles, quantum chemistry, force field simulations and macroscopic differential equations are coupled at different scales. In their strategy, the quantum chemical calculations is applied to study the influence of the active sites of the catalyst, which is followed by Monte Carlo and molecular dynamic simulations of adsorption and diffusion of reactants and products, and ended with continuum modeling of zeolite particles. The main idea in this micro-scale model is to use the results obtained in the simulations at a lower level as an input to the simulations at a higher level. This comprehensive modeling strategy has been demonstrated in the analysis of the diffusion limitation in the alkylation of benzene over H-ZSM-5 crystals (Hansen et al., 2009). Macro-scale models are at highest level for catalyst particles. The main feature of this model is to assume uniform distribution of reaction sites and the same diffusion mechanism inside the whole catalyst particle. In the real catalytic reactors, the reactions over the catalyst pellets are complicated and the diffusion of multi-components needs to be taken into account. So the assumption of uniform distribution can considerably reduce the computational time. The classical approach for predicting the multi-components diffusion and reaction in catalyst pellets is to employ continuum equations with the assumption of the uniform distribution of pore size and active sites in the catalyst pellet (Sahimi, 1990; Hegedus and Pereira, 1990; Solsvik and Jakobsen, 2011, 2012; Keil, 2012; Lim and Dennis, 2012). Solsvik and Jakobsen (2012) recently outlined the derivation of the different diffusion flux models for porous pellets with respect to the molar based and the mass based average velocity definition. The diffusion resistances described by the macro-scale continuum models are in essence the effective resistances which account for the comprehensive effect of the steric resistance and adsorption introduced by the existence of micro-pore crystal particles (active sites). The reaction rates in the continuum models, on other hand, are related to the effective rates where the diffusion within the micro-pore crystal particles is neglected. Therefore, the main problem for macro-scale models is how to effectively predict the diffusion and rate parameters. The key lies in meso-scale models. Since the micro-scale model is related with elementary reaction steps, a meso-scale model embodies important theoretical significance in linking the micro-scale model and macro-scale model.

A meso-scale model could deal with different diffusion mechanisms for different pore sizes. For micro-pore crystal particles, surface diffusion of adsorbed molecular components along the pore wall surface is dominant. The adsorption isotherms and diffusion coefficients within micro-pores could be effectively predicted by means of molecular dynamics and Monte Carlo simulations (Hansen et al., 2009; Hansen and Keil, 2012; Smit and Maesen, 2008). While for macro/meso-pores, the bulk (or molecular) diffusion and Knudsen diffusion becomes important suppose that no strong adsorption exists. In addition, the pressure gradient inside the pellet is not negligible if there is a net change in the number of moles inside the porous catalyst, which can lead to the viscous or Darcy flow in the pellet (Krishna, 1993; Krishna and Wesselingh, 1997). The fluxes of bulk and Knudsen diffusion as well as the viscous flow can be described by a modified Maxwell–Stefan model (Krishna and van Baten, 2009a) in which the gas-phase Maxwell–Stefan diffusion model is modified by introducing the interaction between the species and pore surface or wall. Therefore, it is possible to derive a unified Maxwell–Stefan description for diffusion and/or viscous flow for both micro- and meso-/macro-pores, as shown by Krishna and van Baten (2009b). The main problem for this approach caused by the difference of the diffusion coefficients between macro/meso-pores and micro-pores could be at several orders of magnitude, which means that the diffusion resistance, and thus the characteristic time could be significantly different for these different size pores. In current contribution, we develop a numerical scheme to address this problem.

This paper is organized as following: firstly the unified Maxwell–Stefan diffusion theory is used to describe diffusion and reaction behavior in both micro- and macro/meso-pores in catalyst pellets. Then the multi-region model and corresponding numerical methods are introduced. This model is validated against the results of alkylation of benzene over a single multi-porous pellet formed with H-ZSM-5 crystal particles by Hansen et al. (2009). Finally, the effects of volume fraction, size, and spatial distribution of the H-ZSM-5 crystal particles on the effectiveness factor are studied and discussed.

2. Modeling

2.1. Multi-region model

Our model for reaction–diffusion process in catalyst pellet with multi-pores is a natural outcome of the hierarchical multi-scale idea. From theoretical view, the use of quantum chemical or *ab initio* dynamical simulation can give deep insight into details of a catalytic reaction process with high accuracy. However, the quantum chemical approach, due to its time-consuming characteristic, has been mostly used to calculate energy barriers of elementary reactions and vibration frequency spectrum of stationary geometries along the reaction coordinate (Keil, 2012; Hansen and Keil, 2012). The limited time and length scales in quantum chemical calculation hinder its application in catalyst