

Multi-Scale Modelling of Coke Distribution in MTO process over SAPO-34 Catalyst

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Highlights

- A multi-scale model is developed for multi-scale MTO convection-diffusion-reaction process.
- Coke distribution of a single catalyst particle, and laboratory scale fixed and fluidized bed reactor was simulated.
- The comparison of coke distribution of MTO catalysts in fixed and fluidized bed reactors with experimental data was studied.

1. Introduction

The methanol to olefins (MTO) process provides an alternative approach to produce light olefins from nonoil resources. Industrial MTO catalyst particles contain meso/macro-porous support and micro-porous SAPO-34 zeolite crystals (active sites). In the reactor coke will deposit on the catalysts with reaction proceeding. The coke on the catalyst could affect transport phenomena inside the catalyst pellet, such as reactants adsorption, multi-component diffusion, surface reaction, and reactants and products desorption. It has been pointed out that the conversion of MeOH and product selectivity in MTO process are highly dependent upon the coke content over the MTO catalyst.[1] Investigating the coking mechanism in MTO catalysts is of significant importance to improve the catalytic efficiency of MTO process.

Different pore sizes (micro-pore and meso/macro-pore) inside the MTO catalyst indicate the existence of different diffusion mechanisms.[2] For micro-pore SAPO-34 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[3]. While for meso/macro-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 [4].

In this paper, we developed a multi-scale model to describe the coke formation process, including the diffusion and reaction in micro-pores, diffusion in macro/meso-pores, and convection in the reactor. Different from traditional models for MTO process based upon the assumption of uniform distribution of coke in catalysts, this cross-scale model can deal with zeolite crystal particle to macro-scale laboratory reactor, and predict coke distribution at catalyst pellet and reactor scale by use of kinetics based on dual-cyclic mechanism [5]. The purpose of this work is capable of predicting macro MeOH conversion from a fundamental reaction-diffusion process.

2. Model

In order to address simultaneously the convection-diffusion-reaction process in both micro-pores and macro/meso-pores, we proposed a multi-scale model to deal with different diffusion mechanisms dwelled in different pore sizes. The model is combined with three parts: the kinetic model of MeOH conversion and coke formation [5], the unified Maxwell-Stefan diffusion model, and lab reactor (fixed and fluidized bed) model. Here a simplified model based on dual-cyclic mechanism developed previously used. The details of the multi-scale model is shown in Figure 1.

The corresponding numerical scheme was developed by assuming both zeolite crystal particles and catalyst particles are spherical in shape. 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 combination of Newton iteration, BDF methods, GMRES iteration, and preconditioning method. The simulated results of average coke content at two different positions of a fixed reactor are shown in Figure 1.



Figure 1. The multi-scale model for MTO process.

3. Conclusions

A multi-scale model of MTO process was developed, which provides a potential bottom to up tool for convection-reaction-diffusion processes over SAPO-34 catalyst, which exhibits multi-scale time characteristic. As shown in figure 1, the multi-model covers three scales: zeolite crystal particle, which is about 5 μ m, industrial MTO catalyst particles, which is about 100 μ m, and laboratory reactor, which has dimension of 4-19 mm. The method provides a new tool for catalytic process scale-up, since it can bridge the gap between fundamental reaction mechanisms to practical application.

References

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Keywords

Multi-Scale Model; MTO; Coke Distribution; Porous Catalyst; Convection-Reaction-Diffusion.