EFFECTS OF PORE NETWORK STRUCTURE ON MULTIPHASE REACTIONS USING A DISCRETE MODELLING APPROACH

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Abstract

The effects of pellet size, pore connectivity and pore size distribution on the multiphase reactions at the particle level are investigated by using a discrete model. The proposed discrete model is capable of describing the coupled reaction, mass transfer, capillary condensation, and pore blocking in three-dimensional pore networks reflecting the pore structure of real catalysts; this model is validated by comparing modeling results with experiments on hydrogenation of benzene to cyclohexane in Pd/γ-Al_2O_3 catalysts. Both experiments and simulations display hysteresis of the effectiveness factor as a function of benzene partial pressure in the bulk. Pore connectivity and pore size distribution significantly affect the effectiveness factor and its hysteresis loop area by changes in effective diffusivity and degree of wetting in a catalyst pellet. However, the pellet size only has a significant effect on the effectiveness factor, because pellet size mainly changes the diffusion length. These insights provide useful guidelines for the rational design of industrial porous catalysts for multiphase processes.

Keywords

Pore structure, multiphase reaction, discrete model, three-dimensional pore network, benzene hydrogenation, hysteresis

Introduction

Understanding the effect of pore network structure on catalyst performance is of great importance for the rational design of industrial catalysts. This effect has been comprehensively studied for those reactions without phase change, but less explored for multiphase reactions.

In a catalyst pellet, surface reaction, mass transfer, capillary condensation and pore blocking are intimately coupled, which makes multiphase reactions at the particle level very complicated. As a result, complex phenomena, such as hysteresis in the observed reaction rate or the effectiveness factor, may occur.

Some continuum models have been developed to simulate multiphase reactions in porous catalysts. They are reasonable approximations when pore blocking does not significantly affect multiphase reactions. However, our recent work (Ye et al., 2015) shows that pore blocking effects can be very significant and must be accounted for. Therefore, a discrete model, which is able to include pore blocking, is proposed.

In this contribution, we build a discrete model to probe the effects of pellet size, pore connectivity and pore size distribution on the effectiveness factor under varying reacting conditions, and in particular the hysteresis in the effectiveness factor. Hydrogenation of benzene into cyclohexane is taken as the reaction system, and the catalyst pellet is Pd/γ-Al_2O_3.

Modeling

The proposed discrete model further improves the pioneering work of Wood et al. (2002). The discrete model consists of three tightly connected parts, i.e., a three-dimensional pore network, mass transfer and reaction, and phase change.

Three-dimensional pore networks within a spherical domain are built to reflect not only the pore network structure inside real catalyst pellets but also the pellet shape. This is illustrated in Fig. 1.

Mass transfer and reaction occur simultaneously in the pore network, in the vapor and liquid phases. In the cylindrical pores, the continuity equation is employed:

$$\frac{dJ_{i,n}}{dl_n}\frac{r_n}{2} - R_i = 0 \tag{1}$$

where $J_{i,n}$ is the diffusion flux of component i in pore n, l_n is the length coordinate of pore n, r_n is the radius of pore n, and R_i is the reaction rate per surface area of component i. In the inner nodes, which connect Z pores, Kirchhoff's law is used:

$$\sum_{n=1}^{n=Z} \pi r_n^2 J_{i,n} = 0 \tag{2}$$

For the boundary nodes, a Robin boundary condition is used:

$$-k_i(C_{i,b} - C_{i,boundary}) = J_{i,n} \tag{3}$$

where k_i is the mass transfer coefficient of component i.

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The phase state in each pore can change during the multiphase reaction, which can be described by the theories of capillary condensation and pore blocking. The critical pore radius for capillary condensation is approximated by using the Halsey equation, the Kelvin equation and the Cohan equation. An extended Hoshen-Kopelman algorithm is employed to include pore blocking in this discrete model.

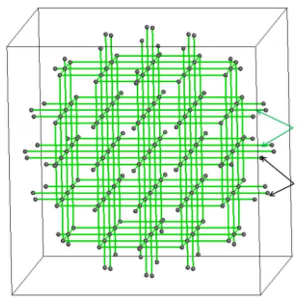

Figure 1. Illustration of three-dimensional, cubic pore networks (connectivity Z=6)

Results and Discussion

Model Validation

The proposed discrete model is validated by comparing with a continuum model and experiments (Zhou et al., 2004). Fig. 2 shows that the effectiveness factors calculated by the discrete model are much closer to experimental ones, illustrating the need to use a discrete model.

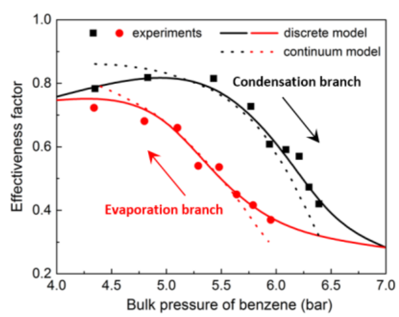

Figure 2. Comparison among the proposed discrete model (this work), the continuum model and experiments (Zhou et al., 2004).

Effects of Pore Network Structure

The pellet radius, pore connectivity, and pore size distribution (i.e., volume-averaged pore radius and standard deviation of a log-normal distribution) are varied to investigate how they affect the effectiveness factor and its hysteresis loop area (S_P). These results are shown in Fig. 3a, Fig. 3b, and Fig. 3c and Fig. 3d, respectively.

Fig. 3 shows that all the aforementioned factors affect the effectiveness factor. Pore connectivity and pore size distribution also change the hysteresis loop area; however, pellet radius only negligibly affects the latter.

Pore connectivity and pore size distribution affect the effective diffusivity and degree of wetting, and subsequently affect both effectiveness factor and its hysteresis loop area; however, pellet radius only affects diffusion length, thus only impacting effectiveness factor.

It is worth noting that when the volume-averaged pore radius and standard deviation are changed, the volume-based activity of the catalyst is also changed. Therefore, when designing industrial catalysts for optimal performance, a compromise among the usage of catalyst (effectiveness factor), the stability of operation (steepness and area of the hysteresis loop), and the reactor volume (the volume-based activity of catalyst) is necessary.

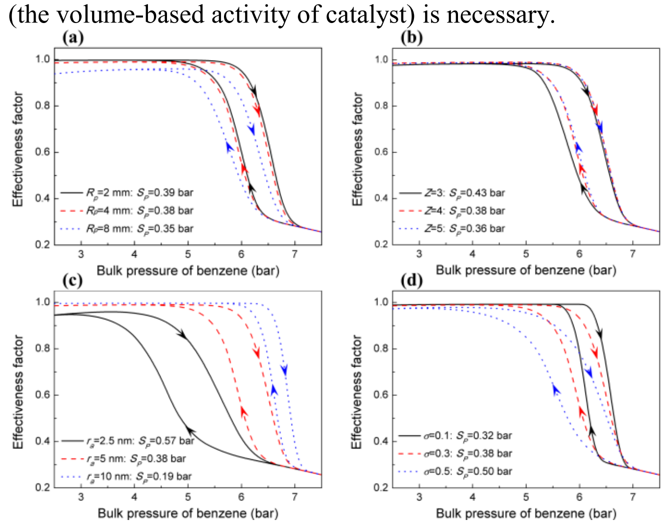

Figure 3. The effects of (a) pellet radius (R_p), (b) pore connectivity (Z), (c) volume-averaged pore radius (r_a), and (d) standard deviation (σ) on the effectiveness factor. The arrows indicate the direction of a change in bulk pressure of benzene.

Conclusions

Pore connectivity and pore size distribution significantly affect the effectiveness factor and its hysteresis loop area; however, pellet size only affects the effectiveness factor. A porous catalyst of small pellet size, high connectivity, large volume-averaged pore radius and narrow pore size distribution performs better in terms of the effectiveness factor. However, for a catalyst with large volume-averaged pore radius and narrow pore size distribution, the hysteresis loop is very steep, which may not be favorable for reactor operation.

Acknowledgments

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