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Crystallite-pore network model of transport and reaction of multicomponent gas mixtures in polycrystalline microporous media

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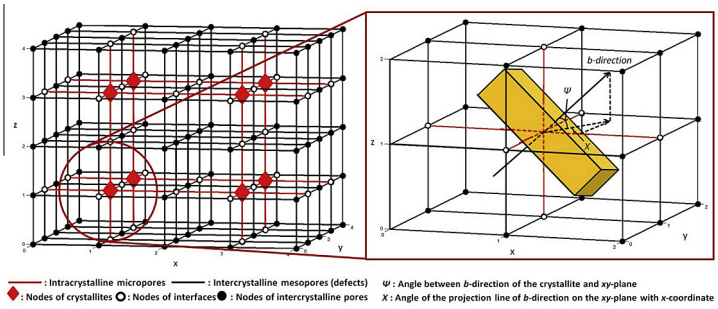
HIGHLIGHTS

- Crystallite-pore network model is proposed to represent polycrystalline media.
- Maxwell–Stefan surface diffusion model is used to simulate transport in micropores.
- Reaction represented by any type of kinetic expressions is allowed in this model.
- Structural effects of polycrystalline media on transport and catalysis are studied.

GRAPHICAL ABSTRACT

Crystallite-pore network model representing polycrystalline microporous media (left), in which the crystallite orientation is described by two angles Ψ and χ (right).



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ABSTRACT

A three-dimensional pore network model has been developed to simulate anisotropic multicomponent diffusion and reaction in polycrystalline microporous media with coexisting intracrystalline micropores and intercrystalline mesopores (i.e., defects). Transport in these pores is modeled with the generalized Maxwell–Stefan surface diffusion model proposed by Krishna [11] and the Knudsen diffusion model, respectively. A new feature highlight of this model is the representation of polycrystalline media with a crystallite-pore network model. In contrast to previous pore network models, the crystallite-pore network model has the novel aspect of modeling the anisotropic transport inside the crystallites forming a polycrystalline layer by assigning to every crystallite two parameters to describe its orientation. The model was applied to simulate xylene isomerization in a polycrystalline ZSM-5 zeolite membrane, which had been experimentally investigated in a Wicke-Kallenbach cell by Haag et al. [13]. First, their experimental data were used to estimate adsorption and diffusion parameters of the xylene isomers in the ZSM-5 membrane *via* fitting single-gas permeance data of the xylene isomers. Second, adopting these parameters, the experimental data for xylene isomerization were used to determine kinetic parameters for xylene isomerization in the ZSM-5 membrane. Finally, effects of selected structural parameters – concentration of defects, connectivity of defects, crystallite orientation, and crystallite size – were investigated using the obtained adsorption, diffusion, and reaction parameters. The simulation results show that high selectivity towards *p*-xylene requires a low concentration of defects in the polycrystalline layer and a low loading of xylene isomers in the membrane. The novel crystallite-pore network model is also applicable to many other reaction systems.

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Nomenclature

A	area, m^2
b	fraction of blocked pores, –
c	concentration, mol/m^3
c	vector of concentration
C	connectivity of intercrystalline pores, –
d	diameter, m
D	diffusion coefficient, m^2/s
D	matrix of diffusion coefficients, m^2/s
E_a	activation energy, kJ/mol
J	molar flow rate, mol/s
J'	molar flow rate after scaling, mol/s
k	reaction rate constant, $m^3/kg/s$
K	adsorption constant, 1/Pa
m	mass, kg
M	molar mass, kg/mol
n	number of components, –
N	molar flux, $mol/m^2/s$
p	pressure, bar
P	connection probability of intercrystalline pores, %
q	loading, mol/kg
r	vector of reaction rates, $mol/m^3/s$
R	universal gas constant, J/mol/K
S	selectivity, –
T	temperature, K
y	mole fraction, –

Subscripts

cry	crystallite
eq	equilibrium
feed	feed gas
inter	intercrystalline
intra	intracrystalline
i, j	component number
K	Knudsen diffusion
memb	membrane
net	network
outside	outside surface of the network
p	pore
sat	saturation
self	self-diffusion
sweep	sweep gas

Superscripts

feed	feed gas
ip	pores connected at the node representing a crystallite
per	permeate side
ret	retentate side
sweep	sweep gas
S	surface diffusion

Greek letters

α	factor of flux distribution in x-, y- and z-coordinate, –
β	mass transfer coefficient, m/s
θ	coverage, –
μ	chemical potential, J/mol
$\boldsymbol{\nu}$	matrix of stoichiometric coefficients, –
ρ	density, kg/m^3
ς	scaling of pore number, –
ψ	angle between the b-direction of crystal and xy-plane, °
χ	angle of the projection line of b-direction on the xy-plane with x-coordinate, °
$\boldsymbol{\Gamma}$	matrix of thermodynamic factors

1. Introduction

Rational catalyst design methodology, which combines computational and experimental approaches, is strongly demanded to reduce the costs of development and improvement of new catalysts. In the last three decades, much attention has been paid to the development of porous heterogeneous catalysts *via* computer-aided optimization of their pore system, since diffusion and reaction processes can be affected significantly by the catalyst pore system.

Pore network models have proven to be a powerful tool to study the effect of the pore system on the catalytic and separation performance of porous media [1–4]. In 1997 Rieckmann and Keil [2] developed a three-dimensional cubic micro–macro pore network model to simulate transport and reaction in the bimodal pore system of pelletized catalysts. Multicomponent transport in a single pore of the pore network was modeled by the dusty-gas model, which combined the contributions of Knudsen diffusion, molecular diffusion and viscous fluxes. As an example, this model was applied in modeling the deactivation of a pelletized ZSM-5 catalyst due to coke formation. In 2008 Chen et al. [4] developed a three-dimensional pore network model to simulate transport and separation of binary gaseous mixtures in amorphous microporous membranes. Compared to Rieckmann and Keil's model, the contributions of hindered and Knudsen diffusion as well as the viscous flux were considered in modeling multicomponent transport of gaseous mixtures in micropores. The results of that article showed that the model was able to predict the single-gas permeances and the ideal selectivity of a silicon-carbide membrane for a helium–argon system.

In recent years, the interest in polycrystalline microporous media for catalysis and separation has grown due to their potential for application in a wide range of industrial processes [5–8]. For instance, due to excellent thermal and chemical stability, polycrystalline microporous zeolite membranes have been applied in fuel cells [7] and membrane reactors [6,8], including catalysis, high temperature separation, and combined catalysis and separation. In order to optimize the separation performance of the zeolite membranes, several one-dimensional models, for example reported in Refs. [9,10], have been used to simulate transport processes in them under the assumption that they are isotropic and homogeneous (pseudo-homogeneous). For example, Van de Graaf et al. [9] used a one-dimensional model to simulate permeation of binary gas mixtures of light alkanes through a silicalite-1 membrane with randomly intergrown crystallites. In that model, multicomponent diffusion in the microporous membrane was simulated with the generalized Maxwell–Stefan Surface Diffusion Model (SDM) proposed by Krishna [11]. The simulation results show that the model is able to predict the permeances of methane and ethane in binary gas mixtures through the silicalite-1 membrane.

In 2003 Lai et al. [12] synthesized a *b*-oriented ZSM-5 membrane and found that it had a superior performance for separation of organic mixtures, such as xylene isomers, compared to conventional membranes with randomly intergrown crystallites. This implies that the orientation of the crystallites can influence the transport in the polycrystalline membranes significantly. The three-dimensional pore network models for the amorphous media as well as the one-dimensional models for the polycrystalline microporous media fail to simulate such anisotropic polycrystalline membranes. In order to simulate the effects of the crystallite