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The effect of pore blockage on the diffusivity in ZSM5: a percolation approach

Antoon O.E. Beyne[1], Gilbert F. Froment*

Laboratorium voor Petrochemische Techniek, Universiteit Gent, Ghent, Belgium

Abstract

The evolution of the effective diffusivity of a pseudo-continuum model of a ZSM5 particle in which progressive blockage occurs is calculated from a network model using bond- and site-percolation theory and the effective medium approximation (EMA). Reduced clusters of varying complexity are evaluated with respect to their capability of accurately predicting the relationship between the evolution of the effective diffusivity with the blockage. A combination of EMA and scaling leads to an excellent agreement with the results of Monte Carlo simulation on a $20 \times 20 \times 20$ lattice. The retained relationship is used in the simulation of reaction and diffusion in a ZSM5 particle of a fixed bed reactor. The catalyst is subject to deactivation by coke formation leading to site coverage and pore blockage.

Keywords: Effective diffusivity; Percolation; Pseudo-continuum model; Effective medium approximation

1. Introduction

Transport phenomena inside solid particles are generally described in terms of a continuum model containing an "effective" diffusivity that combines molecular and Knudsen diffusivities and accounts for the heterogeneous nature of the solid through the porosity, ε, and the tortuosity, τ. The latter expresses the average deviation of the pore orientation with respect to the normal from the surface to the center. This reduces the structure of the particle to that of a single pore or at best to that of a bundle of parallel pores with a distribution in their diameter, but no interconnection. Beeckman et al. [4] and Beeckman and Froment [5–7] represented the internal structure of a catalyst by a tree-like structure, identical to the Bethe-lattice. Tree-like models include interconnection, but there is only one path connecting two points, whereas there may be an infinite number in a real catalyst, in principle at least. Accounting for the latter possibility leads to so-called network models. These require percolation theory to describe the evolution of the accessibility as a function of blockage [2,3,8,9,15–17,20,23,27].

In most networks the accessibility becomes zero before all bonds or sites are blocked. The blockage probability causing zero accessibility is known as the percolation threshold. Bond percolation deals with blockage in the channels or bonds of the network, site percolation with blockage in the channel intersections or nodes. In classical percolation theory, the relationship between the accessibility or percolation probability and the blockage probability is obtained by adding up all the probabilities of occurrence of clusters of various sizes surrounding the origin. This leads to a polynomial approximation including a large number of terms and substantial computational efforts.

The influence of blockage on mass transfer can be modeled using the effective medium approximation (EMA), originally developed by Bruggeman [10] and Landauer [14] as a tool for the estimation of properties of random two-component mixtures. Kirkpatrick [13] further developed the method and applied it as a means to obtain the conductivity of resistor networks from which a fraction of the resistors is removed at random. Essentially, EMA approximates the overall conductivity of a random resistor network by averaging the conductivity of a reduced cluster of bonds or sites in the network. More recent chemical engineering applications were published by Burganos and Sotirchos [11], Sahimi [21] and Zhang and Seaton [26].

The present paper deals with blockage in a zeolite catalyst, more particularly in ZSM5. The blockage affects the accessibility of the active sites and, therefore, the catalyst activity, but also the diffusion pathway of the reacting species, in other words the effective diffusivity. EMA clusters of varying complexity are evaluated with respect to their capability of accurately predicting the relationship between the

* Corresponding author. Present address: Department of Chemical Engineering, Texas A & M University, College Station, TX 77843-3122, USA. *E-mail address:* g.froment@che.tamu.edu (G.F. Froment).

[1] Present address: BASF, D 6700 Ludwigshafen, Germany.

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Nomenclature

C	concentration (kmol/m^3 gas)
$\widehat{C}$	Fourier transformed concentration (kmol/m^3 gas)
$\widehat{C}_C$	particle averaged coke content (kg coke/kg cat × 100)
D	molecular diffusivity (m^2 gas/s)
D_{eff}	effective diffusivity (m^3 gas/m cat/s)
D_{AB}^{C}	total diffusivity between nodes A and B in the composite network (m^2 gas/s)
$D_{\text{AB}}^{\text{eq}}$	total diffusivity between nodes A and B in the equivalent network (m^2 gas/s)
D_{AB}^{h}	diffusivity between nodes A and B in the homogeneous part of the composite network (m^2 gas/s)
l	length of channel segment or lattice constant (m)
$\underline{\underline{M}}$	transformed diffusivity matrix, expresses relation between concentrations and fluxes in the peripheral nodes of the stochastic cluster (m^2 gas/s)
N	molar flux (kmol/m^2 cat/s)
q	blockage probability
q_{cluster}	blockage probability of the stochastic cluster
q_{s}	node blockage probability
r	radial coordinate inside particle (m cat)
R	radius of particle (m cat)
(x, y, r)	coordinates (m, m, m)

Greek symbols

δ	indicator variable, 1 if bond i is opened, 0 if blocked
(ξ, η, ρ)	coordinates in Fourier domain (m^{-1}, m^{-1}, m^{-1})
Λ_{ZSM5}	characteristic function for the ZSM5 lattice

Subscripts

AB	bond AB
eq	equivalent network
i	internal nodes
ij	bond *ij*
p	peripheral nodes
0	indicates the absence of coke or blockage

effective diffusivity and the blockage for both bond- and site percolation. The retained configuration is used in the calculation of the effective diffusivity in ZSM5 catalyzing a process in which the blockage results from coke formation. It is thereby assumed that coke deposition only affects mass transfer if it is blocking the pore in which it occurs. In other words, a decrease of the effective diffusivity due to constriction of the pore cross-section is not considered. This corresponds to a situation encountered when the growth of coke is very rapid with respect to the rate of site coverage.

2. EMA

How are the effective diffusivities of the continuum model representation of a catalyst particle affected by a progressive and random blockage? In the corresponding network model bonds or nodes are randomly blocked and the network is said to be perturbed. The first step consists in the introduction of an equivalent network in which all bonds or nodes are open. The diffusivity in the individual bonds of the equivalent network, referred to as the equivalent diffusivity, D_{eq}, is lower than the diffusivity in the open bonds of the perturbed network, of course. If the blockage probability in the perturbed network increases, the effective diffusivity and the equivalent diffusivity proportionally decrease. The evolution of D_{eq} with respect to its original value, i.e. before blockage occurred, has to be the same as that of the effective diffusivity, D_{eff}.

The objective of EMA is to construct a small size network that permits the derivation of the relation between the diffusivity and the blockage without considering the complete network, thus avoiding the excessive computation this would involve. To this end a composite network is defined. It consists of a homogeneous part, taken from the equivalent network, and a stochastically blocked cluster, which is taken from the perturbed network and whose size has to be optimal.

Let A and B be two nodes in the corresponding perturbed, equivalent and composite networks. Consider a composite network containing a stochastic cluster consisting of one bond, AB. This bond may be opened or blocked, so that its diffusivity is distributed according to the binary distribution.

$$f(D) = q\delta(0) + (1-q)\delta(D - D_0) \tag{1}$$

The presence of the stochastically blocked bond AB causes a disturbance in the flux-concentration pattern of the otherwise homogeneous network. The basic EMA equation states that this disturbance has to averages to zero

$$\left\langle \frac{D_{\text{eq}} - D}{D + D_{\text{AB}}^{\text{h}}} \right\rangle = 0 \tag{2}$$

The solution of this equation is based on the relation between the diffusivity of a channel segment in the equivalent network, D_{eq}, the total diffusivity between nodes A and B in the equivalent network, $D_{\text{AB}}^{\text{eq}}$, and the diffusivity of the homogeneous part of the composite network, D_{AB}^{h}

$$D_{\text{AB}}^{\text{eq}} = D_{\text{eq}} + D_{\text{AB}}^{\text{h}} \tag{3}$$

In the following, a topological description of the ZSM5 catalyst is given first. Then, for bond percolation, EMA is

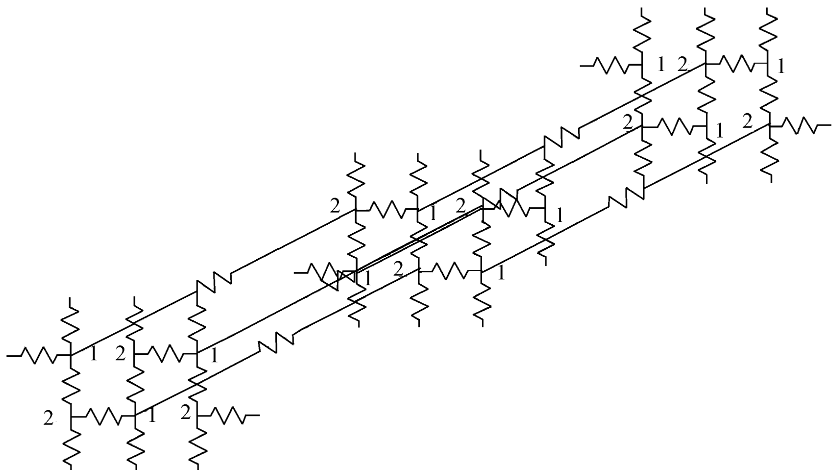

Fig. 1. ZSM5 lattice.

applied to clusters of up to four bonds. The result obtained with the 4-bond cluster is used to model transport and reaction in a ZSM5 catalyst whose channel intersections are progressively blocked, so that the site-percolation approach is required. Switching from bond- to site percolation is straightforward in this case, however.

3. Geometrical representation of ZSM5

The channel structure of ZSM5 is topologically equivalent to that of the diamond lattice for which Gaunt and Sykes (1983) [12] expressed the site-percolation probability in terms of a polynomial of order 20, leading to a site-percolation threshold of 0.5701.

The ZSM5 lattice is composed of two channel types: straight and zigzag. Three main directions can be distinguished in the lattice (Fig. 1). The straight channels are oriented along one of these directions; the zigzag channels are parallel to the two other main directions and are orthogonal to the first direction. The coordination number of the ZSM5 lattice equals 4. In every node, two straight channel segments merge with two zigzag channel segments. In what follows, all channel segments are considered to have equal length.

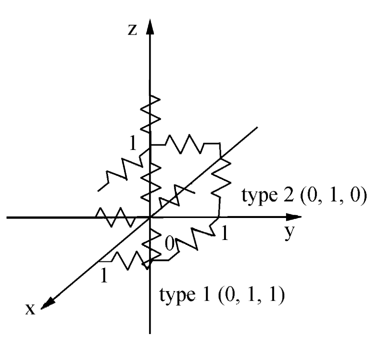

Fig. 2. Coordinate system for ZSM5 lattice.

Two types of nodes are defined, depending upon the position of the neighboring zigzag channels. Type 1 nodes are defined as those nodes in Fig. 1 with one zigzag channel segment to the left and the other one behind; type 2 nodes have their neighboring zigzag channels situated to the right and in front. All neighboring nodes of a type 1 node are of type 2 and vice versa. Concentrations in type 1 nodes are represented as $C^{(1)}$, concentrations in type 2 nodes as $C^{(2)}$. The coordinates of type 1 nodes are represented in the coordinate system of Fig. 2 by $(x, y, 2r - x - y)$, the coordinates of the type 2 nodes by $(x, y, 2r - x - y + 1)$, where x, y and r are integer values. The sum of the coordinates is always even for type 1 nodes and odd for type 2 nodes.

4. Blockage in the catalyst channels

4.1. Stochastic cluster with one bond, oriented along the straight channels

A diffusivity D is attributed to the bond of the stochastic cluster. The value of this diffusivity is stochastically distributed. The end nodes of the bond are written as node 0 and node 1 (Fig. 3). A flux N, directed from 0 to 1, is imposed over the bond.

Let D_{01}^{h} be the diffusivity between the two end nodes 01 in the homogeneous part of the composite network and D_{01}^{eq} the diffusivity in the equivalent network. The diffusivity D_{01}^{h} is related to the equivalent network diffusivity D_{01}^{eq} through Eq. (3).

First, D_{01}^{eq} is calculated as a function of D_{eq}. This is done using the Fourier transformation method. Let node 0 be located in the origin of the network, with coordinates (0, 0, 0) and node 1 be located on the straight channel segment above node 0, having coordinates (0, 0, 1).

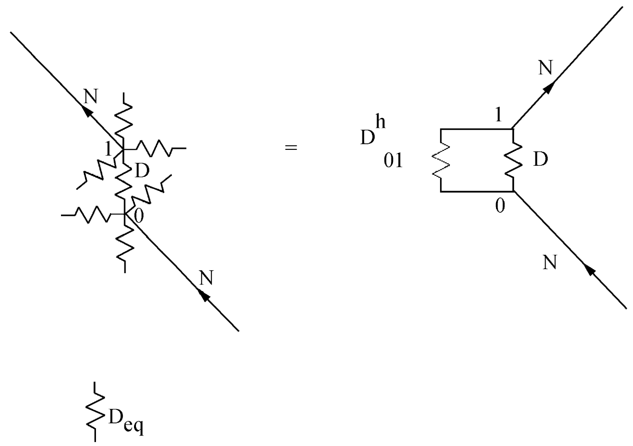

Fig. 3. EMA application to ZSM5 lattice. Stochastic cluster containing one bond along the straight channel.

The material balance over a type 1 node yields

$$\begin{aligned}4C_{\mathrm{eq}}^{(1)}(x,y,2r-x-y)-C_{\mathrm{eq}}^{(2)}(x,y,2r-x-y+1)\\ -C_{\mathrm{eq}}^{(2)}(x,y,2r-x-y-1)-C_{\mathrm{eq}}^{(2)}(x-1,y,2r-x-y)\\ -C_{\mathrm{eq}}^{(2)}(x,y-1,2r-x-y)=\frac{Nl}{D_{\mathrm{eq}}}\delta_{x0}\delta_{y0}\delta_{r0}\end{aligned}\tag{4a}$$

In type 2 nodes, the material balance becomes

$$\begin{aligned}4C_{\mathrm{eq}}^{(2)}(x,y,2r-x-y+1)-C_{\mathrm{eq}}^{(1)}(x,y,2r-x-y+2)\\ -C_{\mathrm{eq}}^{(1)}(x,y,2r-x-y)-C_{\mathrm{eq}}^{(1)}(x+1,y,2r-x-y+1)\\ -C_{\mathrm{eq}}^{(1)}(x,y+1,2r-x-y+1)=-\frac{Nl}{D_{\mathrm{eq}}}\delta_{x0}\delta_{y0}\delta_{r0}\end{aligned}\tag{4b}$$

Fourier transformation leads to the following equations:

$$4\widehat{C}_{\mathrm{eq}}^{(1)}-[1+\mathrm{e}^{-\mathrm{i}\rho}+\mathrm{e}^{-\mathrm{i}(\xi+\rho)}+\mathrm{e}^{-\mathrm{i}(\eta+\rho)}]\widehat{C}_{\mathrm{eq}}^{(2)}=\frac{Nl}{D_{\mathrm{eq}}}\tag{5a}$$

$$-[1+\mathrm{e}^{\mathrm{i}\rho}+\mathrm{e}^{\mathrm{i}(\xi+\rho)}+\mathrm{e}^{\mathrm{i}(\eta+\rho)}]\widehat{C}_{\mathrm{eq}}^{(1)}+4\widehat{C}_{\mathrm{eq}}^{(2)}=-\frac{Nl}{D_{\mathrm{eq}}}\tag{5b}$$

yielding the concentrations $\widehat{C}_{\mathrm{eq}}^{(1)}$ and $\widehat{C}_{\mathrm{eq}}^{(2)}$

$$\widehat{C}_{\mathrm{eq}}^{(1)}(\xi,\eta,\rho)=\frac{Nl}{2D_{\mathrm{eq}}}\frac{3-\mathrm{e}^{-\mathrm{i}\rho}-\mathrm{e}^{-\mathrm{i}(\xi+\rho)}-\mathrm{e}^{-\mathrm{i}(\eta+\rho)}}{\Lambda_{\mathrm{ZSM}}(\xi,\eta,\rho)}\tag{6a}$$

$$\widehat{C}_{\mathrm{eq}}^{(2)}(\xi,\eta,\rho)=-\frac{Nl}{2D_{\mathrm{eq}}}\frac{3-\mathrm{e}^{-\mathrm{i}\rho}-\mathrm{e}^{-\mathrm{i}(\xi+\rho)}-\mathrm{e}^{-\mathrm{i}(\eta+\rho)}}{\Lambda_{\mathrm{ZSM}}(\xi,\eta,\rho)}\tag{6b}$$

The denominator, Λ_{ZSM5}, is characteristic for the ZSM5 lattice

$$\begin{aligned}\Lambda_{\mathrm{ZSM5}}(\xi,\eta,\rho)=6-\cos\xi-\cos\eta-\cos\rho-\cos(\xi-\eta)\\ -\cos(\xi+\rho)-\cos(\eta+\rho)\end{aligned}\tag{7}$$

Finally, D_{01}^{eq} is obtained as a function of D_{eq} by inverse transformation

$$\begin{aligned}\frac{1}{D_{01}^{\mathrm{eq}}}&=\frac{C_{\mathrm{eq}}^{(1)}(0,0,0)-C_{\mathrm{eq}}^{(2)}(0,0,1)}{Nl}\\ &=\frac{1}{D_{\mathrm{eq}}}\frac{1}{(2\Pi)^3}\int_{-\Pi}^{\Pi}\mathrm{d}\xi\int_{-\Pi}^{\Pi}\mathrm{d}\eta\int_{-\Pi}^{\Pi}\mathrm{d}\rho\\ &\quad\times\frac{3-\cos\rho-\cos(\xi+\rho)-\cos(\eta+\rho)}{\Lambda_{\mathrm{ZSM5}}(\xi,\eta,\rho)}\end{aligned}\tag{8}$$

Numerical integration leads to $D_{01}^{\mathrm{eq}}=2D_{\mathrm{eq}}$.

The link between D_{eq} and the blockage probability q is now easily obtained using the classical EMA approach. Eq. (3) shows that the homogeneous network diffusivity, D_{01}^{h}, equals the diffusivity in a bond of the equivalent network, D_{eq}. Substitution of this value into Eq. (2) and introduction of the binary distribution (Eq. (1)) gives a linear relationship between the network diffusivity and the blockage probability

$$\frac{D_{\mathrm{eq}}}{D_0}=1-2q\tag{9}$$

leading to a percolation threshold, q_{C}, of 0.5.

4.2. Stochastic cluster with two adjacent bonds along the straight channels

Before turning to larger stochastic clusters, the EMA approach is applied to a cluster containing two adjacent bonds, oriented along the straight channels. The cluster is represented in Fig. 4. The bonds are indicated as 01 and 03. A flux N enters the cluster at node 1 and leaves it at node 3. Symmetry imposes that the homogeneous network diffusivities D_{01}^{h} and D_{03}^{h} be equal (Fig. 5).

Application of the combination rules for series and parallel connection of conductors gives the following expressions for the diffusivities in the composite network, D_{01}^{C} and D_{13}^{C}:

$$D_{01}^{\mathrm{C}}=D_1+D_{01}^{\mathrm{h}}+\frac{1}{(1/D_{13}^{\mathrm{h}})+(1/(D_3+D_{01}^{\mathrm{h}}))}\tag{10a}$$

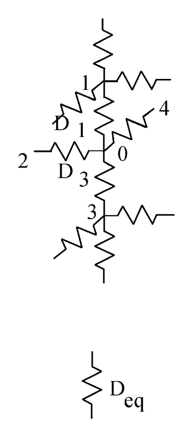

Fig. 4. ZSM5 lattice. Stochastic cluster containing two adjacent bonds oriented along the straight channel.

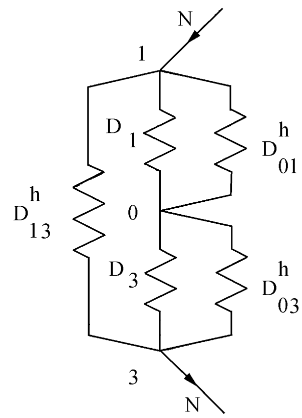

Fig. 5. ZSM5 lattice. Definition of diffusivities in a composite network containing a stochastic cluster with two adjacent bonds along the straight channels.

$$D_{13}^{\mathrm{C}} = D_{13}^{\mathrm{h}} + \frac{1}{(1/(D_1 + D_{01}^{\mathrm{h}})) + (1/(D_3 + D_{03}^{\mathrm{h}}))} \tag{10b}$$

An expression for D_{03}^{C} is obtained by exchanging D_1 and D_3 in Eq. (10a).

In order to obtain the EMA approximation for the equivalent diffusivity D_{eq} the diffusivities in the composite network have to be expressed as a function of D_{eq} and the stochastic variables D_1 and D_3. To that end, a relationship has to be found between the diffusivities D_{01}^{h} and D_{03}^{h} and the equivalent diffusivity D_{eq}.

First, the diffusivities in the equivalent network, D_{01}^{eq}, D_{03}^{eq} and D_{13}^{eq}, are expressed as functions of D_{eq} and the diffusivities D_{01}^{h} and D_{03}^{h}. This is accomplished by setting D_1 and D_3 equal to the equivalent diffusivity D_{eq} in Eqs. (10a) and (10b).

Next, expressions are derived for D_{01}^{eq}, D_{03}^{eq} and D_{13}^{eq} as functions of D_{eq} only. In Section 4.1, it was derived that D_{01}^{eq} equals $2D_{\mathrm{eq}}$. Due to the symmetry of the stochastic cluster, D_{03}^{eq} has the same value. An expression for D_{13}^{eq} is found through Fourier transformed material balances. Using the same network representation as in Section 3, the nodes 0, 1 and 2 are represented by the coordinate triples (0, 0, 0), (0, 0, 1) and $(0, 0, -1)$. The left-hand sides of the material balance equations are identical to those of Eqs. (4a) and (4b), the right-hand sides to 0 for type 1 nodes and to $(Nl/D_{\mathrm{eq}})(\delta_{X0}\delta_{Y0}\delta_{r0} - \delta_{x0}\delta_{y0}\delta_{r,1})$ for type 2 nodes. After Fourier transformation the left-hand sides become equal to those of Eqs. (5a) and (5b), the right-hand sides to 0 and $(Nl/D_{\mathrm{eq}})(l - \mathrm{e}^{\mathrm{i}\rho})$. Solution of this system yields the concentrations in the Fourier domain $\widehat{C}_{\mathrm{eq}}^{(1)}$ and $\widehat{C}_{\mathrm{eq}}^{(2)}$. For type 2 nodes, one obtains

$$\widehat{C}_{\mathrm{eq}}^{(2)} = \frac{2Nl}{D_{\mathrm{eq}}} \frac{1 - \mathrm{e}^{\mathrm{i}\rho}}{\Lambda_{\mathrm{ZSM5}}(\xi, \eta, \rho)} \tag{11}$$

where $\Lambda_{\mathrm{ZSM5}}(\xi, \eta, \rho)$ is given by Eq. (7). The diffusivity D_{13}^{eq} is calculated from

$$\frac{1}{D_{13}^{\mathrm{eq}}} = \frac{C_{\mathrm{eq}}^{(2)}(0,0,1) - C_{\mathrm{eq}}^{(2)}(0,0,-1)}{Nl} = \frac{4}{D_{\mathrm{eq}}} \frac{1}{(2\Pi)^3} \int_{-\Pi}^{\Pi} \mathrm{d}\xi \int_{-\Pi}^{\Pi} \mathrm{d}\eta \int_{-\Pi}^{\Pi} \mathrm{d}\rho \frac{1 - \cos\rho}{\Lambda_{\mathrm{ZSM5}}(\xi, \eta, \rho)} \tag{12}$$

Numerical integration leads to $D_{13}^{\mathrm{eq}} = \frac{3}{2} D_{\mathrm{eq}}$. Similar calculations yield the same result for D_{12}^{eq} and D_{24}^{eq}.

Substitution of the numerical values for D_{01}^{eq}, D_{03}^{eq} and D_{13}^{eq} into Eqs. (10a) and (10b) leads to the following equations for the diffusivities in the homogeneous part of the composite network:

$$D_{01}^{\mathrm{h}} = D_{03}^{\mathrm{h}} = \tfrac{1}{2} D_{\mathrm{eq}}, \qquad D_{13}^{\mathrm{h}} = \tfrac{3}{4} D_{\mathrm{eq}}.$$

Finally, an EMA expression is obtained by imposing that the average concentration difference over the stochastic cluster in the composite network equals the concentration difference over the corresponding cluster in the equivalent network: $\langle \Delta C_{13} \rangle = \langle \Delta C_{13}^{\mathrm{eq}} \rangle$, so that

$$\left\langle \frac{2D_{\mathrm{eq}}^2 + (D_1 + D_3)D_{\mathrm{eq}} - 4D_1 D_3}{4D_{\mathrm{eq}}^2 + 5(D_1 + D_3)D_{\mathrm{eq}} + 4D_1 D_3} \right\rangle = 0 \tag{13}$$

Introduction of the binary diffusivity distribution (Eq. (1)) yields an equation which is quadratic in the blockage probability q and the ratio D_{eq}/D_0

$$9q^2 - 12q\left(\frac{D_{\mathrm{eq}}}{D_0}\right) - 2\left[4\left(\frac{D_{\mathrm{eq}}}{D_0}\right)^2 + \frac{D_{\mathrm{eq}}}{D_0} - 5\right] = 0 \tag{14}$$

Setting the equivalent diffusivity D_{eq} equal to zero yields a value $q_{\mathrm{C}} = 0.5168$ for the percolation threshold.

4.3. *Stochastic cluster with four adjacent bonds*

4.3.1. *Definition of the problem*

Consider a stochastic cluster, consisting of four bonds, 01, 02, 03 and 04 (Fig. 6). These are the bonds adjacent to the origin 0. Let D_1, D_2, D_3 and D_4 be the diffusivities of these bonds. In the composite network, six homogeneous network

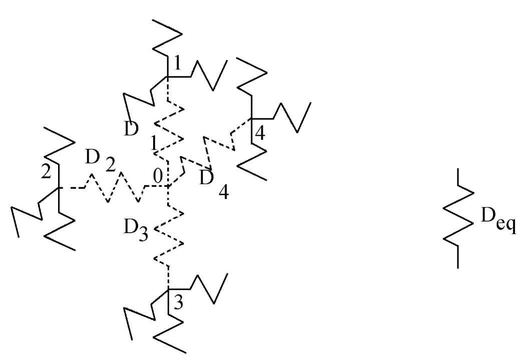

Fig. 6. ZSM5 lattice. Stochastic cluster containing four adjacent bonds.

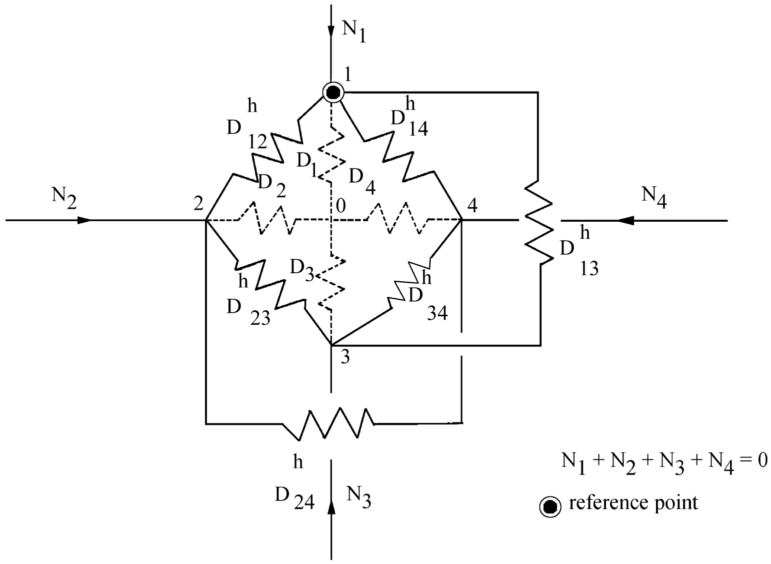

Fig. 7. ZSM5 lattice. Composite network with stochastic cluster containing four adjacent bonds.

diffusivities can be defined: D^{h}_{12}, D^{h}_{13}, D^{h}_{14}, D^{h}_{23}, D^{h}_{24} and D^{h}_{34}. In this set, due to the symmetry of the network, D^{h}_{12}, D^{h}_{14}, D^{h}_{23} and D^{h}_{34} are equal (Fig. 7).

The fluxes, imposed on the composite network, have to satisfy two constraints: there is no flux entering or leaving the network in the origin, node 0, while the sum of all fluxes in the nodes 1, 2, 3 and 4 should equal zero. The first constraint is imposed because all four diffusivities D_1, D_2, D_3 and D_4 may become zero. In that case, the origin is inaccessible and introduction of a constant flux would lead to an infinite concentration difference with respect to the rest of the network. The second constraint results from the steady state, which means that the number of moles of each component remains constant in time.

In matrix notation the material balance equations in the stochastic cluster can be represented by

$$\begin{bmatrix} D_1+D_2+D_3+D_4 & -D_1 & -D_2 & -D_3 & -D_4 \\ -D_1 & D_1+2D^{\mathrm{h}}_{12}+D^{\mathrm{h}}_{13} & -D^{\mathrm{h}}_{12} & -D^{\mathrm{h}}_{13} & -D^{\mathrm{h}}_{12} \\ -D_2 & -D^{\mathrm{h}}_{12} & D_2+2D^{\mathrm{h}}_{12}+D^{\mathrm{h}}_{24} & -D^{\mathrm{h}}_{12} & -D^{\mathrm{h}}_{24} \\ -D_3 & -D^{\mathrm{h}}_{13} & -D^{\mathrm{h}}_{12} & D_3+2D^{\mathrm{h}}_{12}+D^{\mathrm{h}}_{13} & -D^{\mathrm{h}}_{12} \\ -D_4 & -D^{\mathrm{h}}_{12} & -D^{\mathrm{h}}_{24} & -D^{\mathrm{h}}_{12} & D_4+2D^{\mathrm{h}}_{12}+D^{\mathrm{h}}_{24} \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \\ C_4 \end{bmatrix} = l \begin{bmatrix} 0 \\ N_1 \\ N_2 \\ N_3 \\ N_4 \end{bmatrix} \tag{15}$$

4.3.2. Determination of the homogeneous network diffusivities

The homogeneous network diffusivities D^{h}_{12}, D^{h}_{13} and D^{h}_{24} are determined in the equivalent network. The solution procedure can be simplified using the symmetry of the stochastic cluster. A matrix method will be used in the next section to derive the relation between the equivalent diffusivity and the blockage probability.

If a flux N enters the network at node 1 and leaves it at node 3 (Fig. 8), the concentrations C_0, C_2 and C_4 are equal because of the symmetry of the network. This means there is no flux between nodes 0, 2 and 4 and the bonds between these nodes can be deleted. The equivalent network diffusivity D^{h}_{13} can then be calculated using the series and parallel combination rules for conductors:

$$D^{\mathrm{eq}}_{13} = \tfrac{1}{2}D_{\mathrm{eq}} + D^{\mathrm{h}}_{12} + D^{\mathrm{h}}_{13} \tag{16}$$

It was shown in Section 4.2 that $D^{\mathrm{eq}}_{13} = \frac{3}{2}D_{\mathrm{eq}}$, hence

$$D^{\mathrm{h}}_{12} + D^{\mathrm{h}}_{13} = D_{\mathrm{eq}} \tag{17}$$

In an analogous way, in the presence of a flux N directed from node 2 to node 4

$$D^{\mathrm{h}}_{12} + D^{\mathrm{h}}_{24} = D_{\mathrm{eq}} \tag{18}$$

The two preceding equations show that the homogeneous network diffusivities D^{h}_{13} and D^{h}_{24} are equal.

To obtain a third equation for the homogeneous network diffusivities, a flux N, directed from node 1 to node 2, is imposed (Fig. 9). Because of the equivalence of D^{h}_{13} and D^{h}_{24} the flux pattern is symmetrical around the axis connecting the center of the bonds 12 and 34. A material balance over node 1 leads to

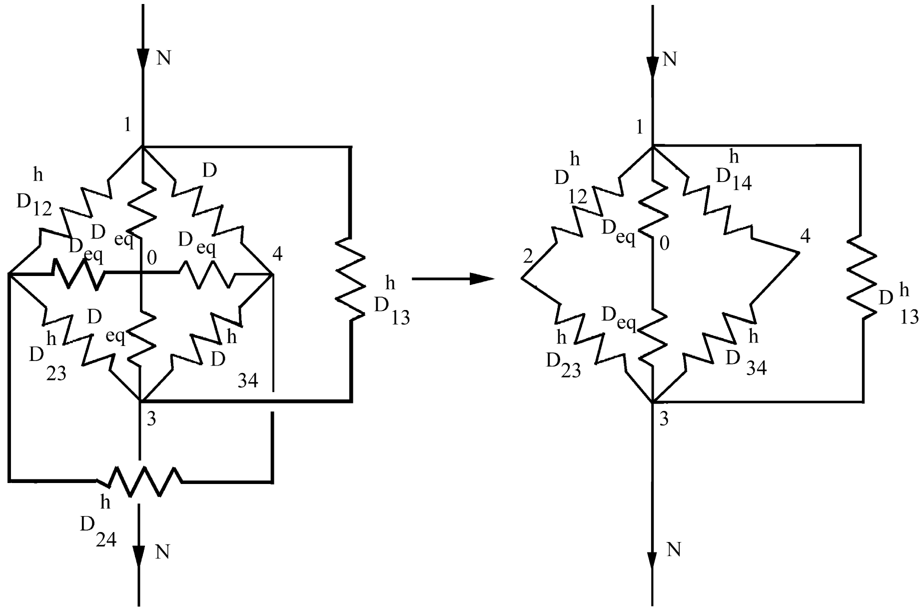

Fig. 8. ZSM5 lattice. Stochastic cluster containing four adjacent bonds, flux pattern with vertical symmetry axis.

$$(2C_{1,\mathrm{eq}} - C_{2,\mathrm{eq}} - C_{4,\mathrm{eq}})D^{\mathrm{h}}_{12} + (C_{1,\mathrm{eq}} - C_{3,\mathrm{eq}})D^{\mathrm{h}}_{13} = Nl - D_{\mathrm{eq}}(C_{1,\mathrm{eq}} - C_{0,\mathrm{eq}}) \tag{19}$$

In Section 4.2, it was pointed out that the equivalent network diffusivity $D^{\mathrm{eq}}_{12} = \frac{3}{2}D_{\mathrm{eq}}$, which means that the concentration difference $C_{1,\mathrm{eq}} - C_{2,\mathrm{eq}}$ equals $\frac{2}{3}(Nl/D_{\mathrm{eq}})$. The concentration difference $C_{1,\mathrm{eq}} - C_{4,\mathrm{eq}}$ is calculated using Fourier transforms. The concentration in a type 2 node is given by

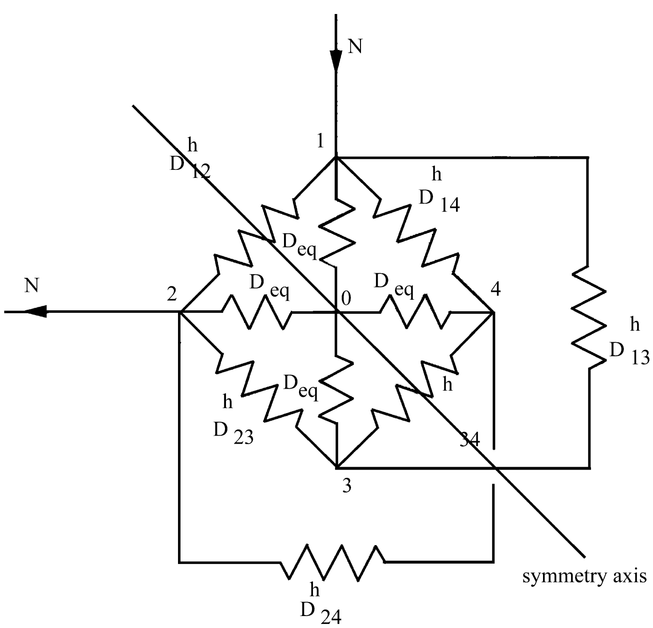

Fig. 9. ZSM5 lattice. Stochastic cluster containing four adjacent bonds, flux pattern with inclined symmetry axis.

$$\widehat{C}^{(2)}_{\mathrm{eq}}(\xi, \eta, \rho) = \frac{2Nl}{D_{\mathrm{eq}}} \frac{1 - \mathrm{e}^{\mathrm{i}(\eta+\rho)}}{\Lambda_{\mathrm{ZSM5}}(\xi, \eta, \rho)} \tag{20}$$

After reverse transformation and numerical integration, $C_{1,\mathrm{eq}} - C_{4,\mathrm{eq}}$ turns out to be $\frac{1}{3}(Nl/D_{\mathrm{eq}})$. Due to the symmetry of the network, the concentration difference $C_{3,\mathrm{eq}} - C_{2,\mathrm{eq}}$ equals $\frac{1}{3}(Nl/D_{\mathrm{eq}})$ as well. Since node 0 is located on the symmetry axis, $C_{0,\mathrm{eq}}$ is equal to the concentration halfway bonds 01 and 34 and the concentration difference $C_{1,\mathrm{eq}} - C_{0,\mathrm{eq}}$ is also given by $\frac{1}{3}(Nl/D_{\mathrm{eq}})$. Substituting these results into Eq. (19) yields

$$D^{\mathrm{h}}_{12} + \tfrac{1}{3}D^{\mathrm{h}}_{13} = \tfrac{2}{3}D_{\mathrm{eq}} \tag{21}$$

and a combination with Eqs. (19) and (20)

$$D^{\mathrm{h}}_{12} = D^{\mathrm{h}}_{13} = D^{\mathrm{h}}_{24} = \tfrac{1}{2}D_{\mathrm{eq}} \tag{22}$$

4.3.3. EMA calculations

The stochastic cluster contains one internal node 0, and four peripheral nodes 1, 2, 3 and 4. Node 1 is chosen as the reference node (Fig. 7). The matrices D_{ii}, D_{pp} and D_{ip} can be written as:

$$\underline{\underline{D}}_{\mathrm{ii}} = [D_1 + D_2 + D_3 + D_4] \tag{23}$$

$$\underline{\underline{D}}_{\mathrm{pp}} = \begin{bmatrix} D_2 + \frac{3}{2}D_{\mathrm{eq}} & -\frac{1}{2}D_{\mathrm{eq}} & -\frac{1}{2}D_{\mathrm{eq}} \\ -\frac{1}{2}D_{\mathrm{eq}} & D_3 + \frac{3}{2}D_{\mathrm{eq}} & -\frac{1}{2}D_{\mathrm{eq}} \\ -\frac{1}{2}D_{\mathrm{eq}} & -\frac{1}{2}D_{\mathrm{eq}} & D_4 + \frac{3}{2}D_{\mathrm{eq}} \end{bmatrix} \tag{24}$$

$$\underline{\underline{D}}_{\mathrm{ip}} = [\, D_2 \quad D_3 \quad D_4 \,] \tag{25}$$

and the $\underline{\underline{M}}$-matrix, upon which the central EMA equation is based on

$$\begin{bmatrix} D_2+\frac{3}{2}D_{\rm eq}-\dfrac{D_2^2}{D_1+D_2+D_3+D_4} & -\frac{1}{2}D_{\rm eq}-\dfrac{D_2D_3}{D_1+D_2+D_3+D_4} & -\frac{1}{2}D_{\rm eq}-\dfrac{D_2D_4}{D_1+D_2+D_3+D_4} \\ -\frac{1}{2}D_{\rm eq}-\dfrac{D_2D_3}{D_1+D_2+D_3+D_4} & D_3+\frac{3}{2}D_{\rm eq}-\dfrac{D_3^2}{D_1+D_2+D_3+D_4} & -\frac{1}{2}D_{\rm eq}-\dfrac{D_3D_4}{D_1+D_2+D_3+D_4} \\ -\frac{1}{2}D_{\rm eq}-\dfrac{D_2D_4}{D_1+D_2+D_3+D_4} & -\frac{1}{2}D_{\rm eq}-\dfrac{D_3D_4}{D_1+D_2+D_3+D_4} & D_4+\frac{3}{2}D_{\rm eq}-\dfrac{D_4^2}{D_1+D_2+D_3+D_4} \end{bmatrix} \tag{26}$$

This matrix is inverted and averaged over all possible configurations of open and blocked bonds in the stochastic cluster. The diffusivities are distributed according to the binary distribution (Eq. (1)). Weighting the inverted $\underline{\underline{M}}$-matrices with their probabilities and requiring the result to equal the inverted $\underline{\underline{M}}_{\rm eq}$-matrix yields the following relationship between the equivalent diffusivity and the blockage probability

$$\frac{D_{\rm eq}}{D_0}=1-\frac{1}{2}(4-q^3) \tag{27}$$

where $D_{\rm eq}$ becomes zero at the critical blockage probability $q_{\rm C}$, for which an approximate value of 0.5180 is obtained.

The approximation of $q_{\rm C}$ in the bond-percolation problem on a diamond lattice, arrived at by using EMA, differs significantly from the exact value of 0.612 (Gaunt and Sykes,1983; [12]). EMA is most accurate for predicting the evolution of the effective diffusivity with the blockage probability for relatively low and medium values of the latter [26]. An extension called renormalized EMA [18,19,22] significantly improves the accuracy over the entire range of blockage. It will be shown below that a combination of EMA and scaling yields excellent approximations over the entire range of blockage probabilities.

5. Blockage in the catalyst channel intersections

In this section, the evolution of the effective diffusivity is modeled as a function of the fraction of blocked nodes. This requires that the results obtained in the preceding paragraphs for bond percolation, have to be adapted to the site-percolation problem. This will be done first for a stochastic cluster containing one internal node.

5.1. Stochastic cluster with one internal node

Consider the stochastic cluster used in Section 4.3 for the description of the effective diffusivity as a function of the bond blockage probability. This cluster contains one internal node surrounded by four bonds. In bond percolation, the properties of the stochastic cluster are determined by the bonds of the cluster, in site percolation by the central node. Each element of the stochastic cluster can be in two states: it can be opened or blocked. The state of an element is independent of the states of the other elements. Consequently, the number of possible states of the stochastic cluster itself equals 2 raised to a power corresponding to the number of cluster elements. The cluster considered here contains four bonds and one node. In bond percolation it can be in $2^4=16$ different states, in site percolation in $2^1=2$ states only.

Let the $\underline{\underline{M}}$-matrix for the cluster containing one open node be represented by $\underline{\underline{M}}(1)$ and that for the cluster containing one blocked node by $\underline{\underline{M}}(0)$. The basic EMA equation then becomes

$$[\underline{\underline{D}}_{\rm pp}-(\underline{\underline{D}}_{\rm ip})^{\rm T}(\underline{\underline{D}}_{\rm ii})^{-1}\underline{\underline{D}}_{\rm ip}]^{-1} = [\underline{\underline{D}}^{\rm eq}_{\rm pp}-(\underline{\underline{D}}^{\rm eq}_{\rm ip})^{\rm T}(\underline{\underline{D}}^{\rm eq}_{\rm ii})^{-1}\underline{\underline{D}}^{\rm eq}_{\rm ip}]^{-1} \tag{28}$$

The state of the bonds in the cluster is now determined by the state of the central node. If it is open, all surrounding bonds are open; if it is blocked, all surrounding bonds are blocked. This means that matrix $\underline{\underline{M}}(1)$ equals matrix $\underline{\underline{M}}(1,1,1,1)$ of the bond-percolation problem discussed in Section 4.3. Matrix $\underline{\underline{M}}(0)$ equals matrix $\underline{\underline{M}}(0,0,0,0)$. The equivalent matrix $\underline{\underline{M}}^{\rm eq}$ remains unchanged. A linear relationship between the equivalent diffusivity and the blockage probability is derived

$$\frac{D_{\rm eq}}{D_0}=1-\frac{3}{2}q \tag{29}$$

This equation yields an approximate percolation threshold $q_{\rm C}$ of $\frac{2}{3}$, which differs considerably from the value of 0.5701, mentioned by Stauffer and Aharony [24] for site percolation on the diamond lattice. The evolution of the effective diffusivity with the blockage probability also differs significantly from that obtained by means of Monte Carlo simulation on a $20\times20\times20$ lattice (Fig. 10).

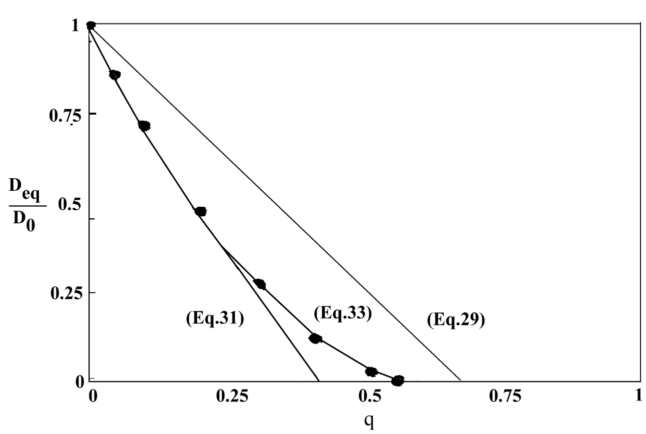

Fig. 10. Equivalent diffusivities for site percolation in ZSM5. Comparison of EMA results (curves) with Monte Carlo simulation on a $20\times20\times20$ lattice (dots).

Applying EMA to a stochastic cluster with two internal nodes requires lengthy and tedious calculations and did not improve the approximation, probably due to the lower symmetry of this cluster. Ahmed and Blackman (1979) [1] pointed out that the cluster has to include the "essential correlation". At low values of the blockage probability the blockage of a bond or site only affects the vicinity and a small cluster suffices to account for that. This is not the case any more close to the percolation threshold, where the density of accessible sites is significantly lower and the blockage of a site may affect the accessibility of remote sites. A different type of cluster is required.

5.2. Stochastic cluster with one internal and one peripheral node

The above results can be improved by taking into account the peripheral nodes of the cluster. The stochastic cluster with one internal node contains four peripheral nodes as well. If the network is divided into similar clusters, then each peripheral node is also part of four neighboring clusters (Fig. 9). This means that; in addition to the central node, the stochastic cluster contains $4 \times \frac{1}{4} = 1$ peripheral node. Hence, the stochastic cluster contains two nodes instead of one. Fig. 9 shows another representation of the stochastic cluster in which the cluster contains two complete nodes. In Eq. (29), the probability that the central intersection is blocked should be replaced by the probability that the cluster is blocked. The cluster is blocked if at least one node is blocked. The blockage probability of a cluster with two nodes is given by

$$q_{\text{cluster}} = 1 - (1 - q_{\text{s}})^2 = q_{\text{s}}(2 - q_{\text{s}}) \tag{30}$$

Eq. (29) becomes

$$\frac{D_{\text{eq}}}{D_0} = 1 - 3q_{\text{s}} + \frac{3}{2}q_{\text{s}}^2 \tag{31}$$

The trend reflected by this equation was already observed, e.g. by Watson and Leath [25]. Eq. (31) leads to a threshold value of 0.52. Fig. 10 shows that the equation reproduces the Monte Carlo simulations almost perfectly for blockage probabilities up to 0.25, for which D_{eq}/D_0 is larger than 0.4, but not in the vicinity of the percolation threshold.

5.3. Combination with scaling

Near the percolation threshold, the evolution of the equivalent diffusivity is described by a scaling law with critical exponent 2 (Stauffer and Aharoni [24]). The final approximation for the evolution of the equivalent diffusivity with the blockage probability is obtained in two steps. First, Eq. (31) is divided by the critical term $(l - q/q_{\text{C}})^2$, yielding the quotient series

$$\frac{1 - 3q_{\text{s}} + (3/2)q_{\text{s}}^2}{[1 - (q_{\text{s}}/q_{\text{C}})]^2} = 1 + \left(\frac{2}{q_{\text{C}}} - 3\right) q_{\text{s}} + \left(\frac{3}{q_{\text{C}}^2} - \frac{6}{q_{\text{C}}} + \frac{3}{2}\right) q_{\text{s}}^2 + \cdots \tag{32}$$

Truncating the series after the second-order term and multiplying it again with the critical term yields the following expression, combining EMA with scaling

$$\frac{D_{\text{eq}}}{D_0} = \left[1 - \frac{q_{\text{s}}}{q_{\text{C}}}\right]^2 \times \left[1 + \left(\frac{2}{q_{\text{C}}} - 3\right) q_{\text{s}} + \left(\frac{3}{q_{\text{C}}^2} - \frac{6}{q_{\text{C}}} + \frac{3}{2}\right) q_{\text{s}}^2\right] \tag{33}$$

in which $q_{\text{C}} = 0.5701$, according to the accessibility–blockage relationship derived by Gaunt and Sykes (1983) for site percolation in the diamond lattice.

This equation fits the Monte Carlo results almost exactly over the entire range of blockage probabilities (Fig. 10). According to the EMA principle the same formula holds for the evolution of $D_{\text{eff}}/D_{\text{eff},0}$,which is the ratio entering into the application of the pseudo-continuum model.

6. An example of application

Eq. (33) has been applied by Beyne and Froment [7,8] in the calculation of the evolution of the effective diffusivities in a pseudo-continuum model of a ZSM5 catalyst for a chemical process carried out in a fixed bed reactor. The process consists of a main reaction A → B with a rate determining step A1 → B1 involving species adsorbed on single sites and is subject to diffusional limitations. Coke is formed out of A (parallel coking) or B (consecutive coking) and involves irreversible site coverage followed by growth leading to pore

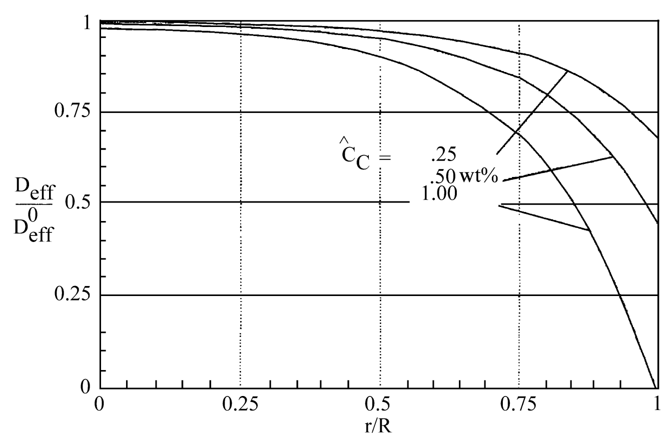

Fig. 11. Evolution of $D_{\text{eff}}/D_{\text{eff},0}$ inside a ZSM5 particle with the coke content parallel coking.

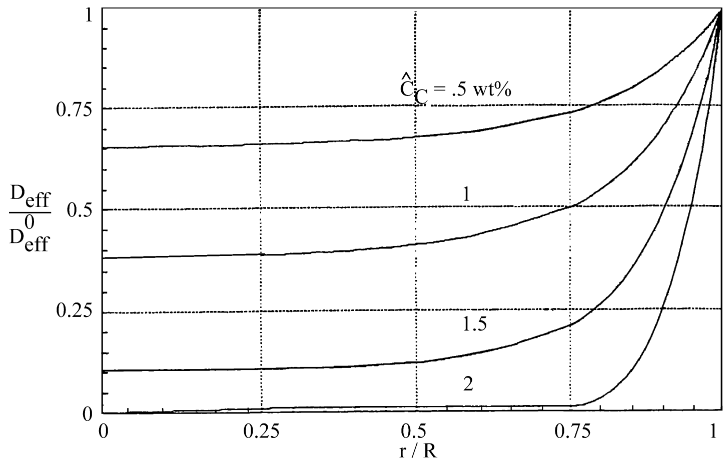

Fig. 12. Evolution of $D_{\mathrm{eff}}/D_{\mathrm{eff},0}$ inside a ZSM5 particle with the coke content consecutive coking.

blockage. In the case dealt with here the rate determining step in the coke production is the irreversible site coverage, so that the coke growth may be considered to be instantaneous and leading to coke particles with identical size, that of the channel diameter. The rate equations are derived using the Hougen–Watson approach and contain deactivation functions accounting for site coverage and pore blockage. The effect of pore blockage on the effective diffusivity for A in a particle located in a cross-section at a certain distance from the bed inlet is shown in Fig. 11 for parallel coking and in Fig. 12 for consecutive coking. The profiles of $D_{\mathrm{eff}}/D_{\mathrm{eff},0}$ follow those of the coke: with parallel coking, the local coke content is highest at the surface and this is where the effect of blockage on the effective diffusivity is more pronounced, whereas with consecutive coking the effect is strongest in the core.

7. Conclusions

The present paper describes the application of the EMA method in modeling the evolution of the effective diffusivity with the blockage probability in a ZSM5 lattice. The application was developed for both bond- and site percolation. Formulae were derived for stochastic clusters containing up to four bonds in the bond-percolation problem and for stochastic clusters containing one internal node or one internal and one peripheral node in the site-percolation problem. Their accuracy was evaluated by comparison with literature data and Monte Carlo simulation.

The combination of EMA with scaling significantly improves the prediction and yields an excellent approximation of the evolution of the effective diffusivities with blockage over the entire range of blockage probabilities. When inserted into a pseudo-continuum model for transport and reaction inside a catalyst particle this relationship definitely improves the accuracy of such a model, which is widely used in reactor simulation, given its simplicity relative to truly discrete or heterogeneous particle models.

References

[1] G. Ahmed, J.A. Blackman, J. Physics. 12 (1979) 837.
[2] S. Arbabi, M. Sahimi, Chem. Eng. Sci. 46 (7) (1991) 1739.
[3] S. Arbabi, M. Sahimi, Chem. Eng. Sci. 46 (7) (1991) 1749.
[4] J.W. Beeckman, G.F. Froment, L. Pismen, Chem. Ing. Technol. 50 (12) (1978) 960.
[5] J.W. Beeckman, G.F. Froment, Ind. Eng. Chem. Fund. 18 (3) (1979) 245.
[6] J.W. Beeckman, G.F. Froment, Chem. Eng. Sci. 35 (1980) 805.
[7] J.W. Beeckman, G.F. Froment, Ind. Eng. Chem. Fund. 21 (1982) 243.
[8] A.O.E. Beyne, G.F. Froment, Chem. Eng. Sci. 45 (8) (1990) 2089.
[9] A.O.E. Beyne, G.F. Froment, Chem. Eng. Sci. 48 (3) (1993) 503.
[10] D.A.G. Bruggeman, Ann. Phys. (Leipzig) 24 (1935) 636.
[11] V.N. Burganos, S.V. Sotirchos, AIChEJ 33 (10) (1987) 1678.
[12] D.S. Gaunt, M.F. Sykes, J. Phys. A 16 (1983) 783.
[13] S. Kirkpatrick, Rev. Mod. Phys. 45 (4) (1973) 574.
[14] K. Landauer, J. Appl. Phys. 23 (7) (1952) 779.
[15] R.R. Melkote, K.F. Jensen, Chem. Eng. Sci. 44 (3) (1989) 649.
[16] K.K. Mohanty, J.M. Ottino, H.T. Davis, Chem. Eng. Sci. 37 (6) (1982) 905.
[17] W.T. Mo, J. Wei, Chem. Eng. Sci. 41 (1986) 703.
[18] M. Sahimi, B.D. Hughes, L.E. Scriven, H.T. Davis, Phys. Rev. B 28 (1) (1983) 307.
[19] M. Sahimi, L.E. Scriven, H.T. Davis, J. Phys. C 17 (1984) 1941.
[20] M. Sahimi, T.T. Tsotsis, J. Cata. 3/4o96 (1985) 552.
[21] M. Sahimi, Chem. Eng. Commun. 64 (1988) 177.
[22] M. Sahimi, Applications of Percolation Theory, Taylor and Francis, London, 1994.
[23] N. Shah, J.M. Ottino, Chem. Eng. Sci. 42 (1) (1987) 73.
[24] D. Stauffer, A. Aharony, Introduction to Percolation Theory, 2nd Edition, Taylor and Francis, London, 1992.
[25] B.P. Watson, P.L. Leath, Phys. Rev. B 9 (1974) 4893.
[26] L. Zhang, N.A. Seaton, AIChEJ 38 (11) (1992) 1816.
[27] V.P. Zhdanov, Catal. Lett. 9 (1991) 369.