Dynamic Monte-Carlo simulations of diffusion limited reactions in rough nanopores

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Abstract

It has recently been demonstrated that self- (or tracer) diffusivities and transport diffusivities of gases in nanoporous materials may differ in the Knudsen regime, when the pore surface is rough on molecular scales. Self-diffusion is roughness dependent, while transport diffusion is not. The impact of this result on diffusion-controlled reactions, catalysed by porous catalysts with a rough internal surface, is now investigated. We consider the steady state problem of a species diffusing in a three-dimensional pore with a fractal surface, on which the species reacts. Dynamic Monte-Carlo simulations and analytical calculations show that the self-diffusivity plays the fundamental role in determining the effective catalytic efficiency of a rough pore. The transport diffusivity, on the other hand, is not the fundamental quantity of interest to surface phenomena such as heterogeneous catalysis, and can only be used for porous materials with a smooth internal surface, in which case the self- and transport diffusivities coincide.

Keywords: dynamic Monte-Carlo; diffusion; reaction; fractals; nanoporous materials

1. Introduction

The study of transport phenomena in porous media is a long-standing research subject with many industrial and technological applications (Aris, 1975, 1989; Adler, 1992). The improvement of models to describe diffusion and reaction in heterogeneous catalysts constitutes a real challenge, due to the complexity of the texture of porous catalysts and the limitations of classical, continuum representations (Froment and Bischoff, 1990; Sahimi, Gavalas and Tsotsis, 1990). Considerable effort has therefore been

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dedicated to the investigation of diffusion and reaction in complex geometries, involving topologically or morphologically irregular pore networks (see, *e.g.*, reviews by Sahimi, Gavalas and Tsotsis, 1990; Burganos, 1993, 1998; Keil, 1999). Nevertheless, the roles played by the pore shape and the local surface morphology on the overall diffusivity and, hereby, on the effective activity of a catalyst remain to be better understood.

Many amorphous porous catalysts and catalyst supports have a fractal internal surface (Pfeifer and Avnir, 1983; Avnir, Farin and Pfeifer, 1984). Consequently, several groups have studied the role played by the fractal roughness of a surface on its accessibility to diffusing molecules that react on it, and on the overall reaction rate (Meakin, 1986; Pajkossy and Niykos, 1989; Gutfraind, Sheintuch and Avnir, 1991; Gutfraind and Sheintuch, 1992; Coppens and Froment, 1994, 1995a, 1995b; Pfeifer and Sapoval, 1995; Mougin, Pons and Villiermaux, 1996; Sapoval, Andrade and Filoche, 2001). Surface roughness of porous materials affects the trajectories of molecules diffusing through the pores, in particular in the Knudsen diffusion regime, since diffusion then involves molecular motions between points on the pore walls (Coppens, 1999). Fractal pore models were used to study the effect of surface roughness on Knudsen diffusion (Coppens and Froment, 1995c; Santra and Sapoval, 1998), but the conclusions were different, some researchers observing effects and others not. In order to investigate this apparent disagreement, Malek and Coppens (2001, 2002) recently performed dynamic Monte Carlo simulations and analytical calculations in two- and three-dimensional rough pores. This work resolves the discrepancy, by demonstrating that there is a fundamental difference between gradientless *self-* or *tracer* diffusion, on the one hand, and *transport* diffusion, *i.e.*, diffusion under the influence of a concentration gradient, on the other: the former is roughness dependent and well described by the analytical predictions by Coppens and Froment (1995c), while the latter is roughness independent. The decrease of the self-diffusivity with increasing roughness is especially significant in pores that are rough over a range from molecular scales up to scales on the order of the average pore diameter, a realistic range in catalysis (Coppens, 2001). Figure 1(a) summarizes these results for a three-dimensional model pore with a random self-similar fractal surface generated through the iterative rule displayed in Figure 1(b); the irregularity or roughness factor of the pore at any level of its fractal generation, ξ , is given by the ratio of the pore boundary length (2D) or surface area (3D) to the pore boundary length or surface area of an unperturbed smooth pore with the same cross-section, *i.e.*, a smooth pore with a square cross-section.

Differences between self- and transport diffusion are well documented for zeolites (Kärger and Ruthven, 1992; Keil, Krishna and Coppens, 2000), but not for mesoporous materials, where it has generally been assumed that they are the same. It appears, however, that any hindrance or “trapping” phenomenon leads to such a difference, whether it is by molecules hindering each other’s motion during activated, hopping diffusion in microporous zeolites or by surface roughness hindering the Knudsen diffusion of molecules in mesoporous materials. The large effect of roughness on self-diffusion occurs because the self-diffusivity, D_K^s , is a direct function of the individual molecular trajectories, the total trajectory length or residence time, and therefore decreases significantly as the roughness factor, ξ , increases. The transport diffusivity, D_K^t , on the other hand, does not vary with ξ , *i.e.*, it does not depend on roughness, because it only depends on the (roughness independent) transmission probability, which is the probability for molecules to leave the pore on one side when they moved in through the other.

In light of these recent results, this paper reconsiders the effect of surface roughness on a Knudsen diffusion-limited reaction, using dynamic Monte-Carlo simulations and analytical calculations. Reactant molecules “injected” into a pore move through the pore space and collide with the walls until they make an effective collision with an active site where they react to form product molecules. Whatever hinders or aids the motion (*e.g.*, surface roughness, adsorption) will affect a molecular trajectory, the collision rate and the probability to react. Arguably, the *self-diffusivity*, which evaluates by means of Einstein’s relation how the variance of the position of a molecule changes over time, is therefore the more fundamental diffusivity in heterogeneous catalysis, since it is directly related to the molecular trajectories. Dynamic Monte-Carlo is a good tool to investigate this issue. Yet the most frequently used models in catalysis and reaction engineering use continuity equations for the components that involve Stefan-Maxwell’s or Fick’s equations to describe diffusion (Froment and Bischoff, 1990). These descriptions, at least *formally*, appear to be based upon *transport diffusivities*, which, as shown earlier, are different from self-diffusivities for rough pores. This raises the question whether self- or transport diffusivities should be used in evaluating the yield of a diffusion-limited reaction. Another question is whether the diffusivity is even the same in the presence of reaction as in its absence. If they are different, the diffusivity evaluated in the absence of reaction may not be used as such in a relation expressing yields as a function of intrinsic kinetics and “pure” diffusivities. Work by, amongst others, Cui *et al.* (1990), Weisz (1995), and Reyes, Sinfelt and DeMartin (2000), indicates that this could

sometimes be the case. Since a fractal surface is not uniformly accessible to diffusing molecules, this non-uniform accessibility distribution may in principle influence the effective reaction rates through a surface effectiveness factor $\eta^s < 1$.

2. Continuum description of Knudsen diffusion and reaction in a fractal pore

Coppens and Froment (1995a, 1995b) studied the influence of the fractal surface morphology on Knudsen diffusion and reaction in a fractal pore, and applied this model to industrial processes such as the production of vinyl acetate (Coppens and Froment, 1994) and the catalytic reforming of naphtha (Coppens and Froment, 1996; Coppens, 1999). In this continuum model, they used relations for the Knudsen diffusivity as a function of fractal surface roughness and molecule size that were derived in the absence of reaction (Coppens and Froment, 1995b, 1995c). For a fractal self-similar surface with fractal (adsorption) dimension D_{ads} and outer cutoff δ_{max} (the upper boundary of the fractal scaling regime), a mean-field approximation predicts the Knudsen diffusivity D_K^s to be inversely proportional to the accessible surface area:

$$D_K^s = D_{K0} (\delta')^{D_{ads}-2} \quad (1),$$

in which D_{K0} is the Knudsen diffusivity in a smooth porous medium with the same pore network topology and smoothened pore shapes as the real, rough medium, and $\delta' = \delta / \delta_{max}$ is the normalized effective diameter of a molecule of size δ (Coppens and Froment, 1995b). This relation is based upon the fact that the area of a fractal surface accessible to molecules of size δ increases with decreasing δ as a power law $(\delta')^{2-D_{ads}}$ within the fractal scaling regime (Pfeifer and Avnir, 1983). The non-uniform accessibility of the surface can be accounted for by a model that uses a first-passage time approach, leading to the following, more accurate expression for the Knudsen diffusivity (Coppens and Froment, 1995c; Malek and Coppens, 2001):

$$D_K^s = \frac{D_{K0}}{1 + \alpha [1 - (\delta')^\beta]} \quad (2),$$

in which α and β are constants that can be calculated from the fractal adsorption dimension of the surface, D_{ads} , and a parameter p_0 , the so-called return probability, *i.e.*, the probability for a molecule to leave a

fjord or indentation along the surface it has entered before. Coppens and Froment (1995c) and Malek and Coppens (2001) give simple analytical expressions for $\alpha(D_{ads}, p_0)$ and $\beta(D_{ads}, p_0)$ in two and three dimensions. Malek and Coppens (2001) show that this relation is only valid for the self-diffusivity, D_K^s , while the transport diffusivity, D_K^t , is roughness independent, *i.e.*, $D_K^t = D_{K0}$.

In order to solve the problem of diffusion and reaction in a rough pore using a continuum approximation, some adaptations to the original model of Coppens and Froment (1994, 1995b) need to be made that allow extending the validity of the results to very fast reactions, so that these results can be compared to the dynamic Monte-Carlo simulation results in Section 3. Indeed, Monte-Carlo simulations are typically carried out for nanopores that are only up to a few hundred times longer than their diameter (order of ~ 100 nm to μm), so that diffusion limitations can only be observed for extremely fast reactions. Such pores are much longer than the outer cutoff of the fractal scaling regime, making a continuum model meaningful, yet they are shorter than a typical catalyst particle size. As will become clear further on, the better-known continuum approach with Dirichlet boundary conditions is no longer valid at these scales, but can be quite easily extended. It is mentioned *a priori* that the procedure used here can be used to compare dynamic Monte-Carlo simulations with continuum models in general, not only in the framework of pore roughness.

Consider an open pore of axial length $z_{\max} = 2L \geq \delta_{\max}$ and constant cross-sectional surface area Ω (Figure 2). A gaseous species A diffuses through this pore and is converted on its fractal walls to an isomer B by means of a single first-order reaction with intrinsic kinetics $r_A = k C_A$. Like in earlier work, a pore model is used to isolate the problem of studying the influence of surface morphology from effects resulting from pore network topology. While not essential at this stage, it is further assumed that the mean free path of A and B is larger than the pore diameter, so that the mixture is in the Knudsen regime. This implies that A and B diffuse independently from each other. The Knudsen diffusivity of A is denoted by D_K , where it is not specified for the time being whether this is the self-diffusivity, D_K^s , or the transport diffusivity, D_K^t . For smooth pores, $D_K^t = D_K^s$. A classical chemical engineering approach is used to evaluate the concentration profile and the conversion of A as a function of the fractal dimension of the surface, D_{ads} . A one-dimensional model is used, with equations projected along the pore axis z . The imposed concentration of A at both pore ends is C_A^0 , so that the problem is symmetric and the flux in

the centre ($z=L$) is zero. However, care has to be taken in formulating the correct boundary condition for $z=0$, which becomes especially important when comparing the results with Monte-Carlo simulations further on. There may indeed be a jump in concentration at the pore entrance, so that the concentration $C_A(0^+)$ is, in general, not equal to $C_A^0=C_A(0^-)$, the concentration immediately outside of the pore. The number of moles entering the pore, at $z=0$, per unit of area and per unit of time is given by $C_A^0 \bar{u} / 4$, $\bar{u}$ being the average molecular velocity. At $z=0$ the net inward flux equals this imposed inward molecular flux minus the outward molecular flux $C_A(0^+) \bar{u} / 4$, corresponding to the concentration immediately inside the pore, at the pore entrance, $C_A(0^+)$. The boundary conditions therefore become:

$$\begin{aligned} -D_K \frac{dC_A}{dz} + \frac{C_A \bar{u}}{4} \Big|_{z \rightarrow 0^+} &= \frac{C_A^0 \bar{u}}{4} \\ \frac{dC_A}{dz}(z=L) &= 0 \end{aligned} \quad (3).$$

The first boundary condition, a direct result of the above statistical description, can also be interpreted as an external mass transfer limitation with a mass transfer coefficient equal to $\bar{u} / 4$ (Aris, 1975). The dimensionless continuity equation for component A is given by:

$$\frac{d^2(C_A / C_A^0)}{d(z/L)^2} = \Phi^2 (C_A / C_A^0) \quad (4),$$

in which the Thiele modulus for the pore is:

$$\Phi = L \sqrt{\frac{\eta^s k \rho_s}{D_K}} \quad (5),$$

in which η^s is the surface effectiveness factor, which describes concentration gradients as a result of surface roughness, perpendicular to the pore axis, and can be shown to be approximately 1 in most cases. Depending on the situation, either the reaction rate constant on a mass basis, k ($\text{m}^3/\text{kg}_{\text{cat}}\text{s}$), or the reaction rate constant on a surface area basis, k_s ($\text{m}^3/\text{m}^2_{\text{cat}}\text{s}$), may be known. The relation between both is the specific surface area a ($\text{m}^2_{\text{cat}}/\text{kg}_{\text{cat}}$) accessible to the reacting molecules: $k = k_s a$. This distinction is important when comparing fractal and smooth pores, for which not only the diffusivity [eq. (2)], but also the reaction rate constant k may differ, when situations with the same k_s are compared. In the latter case $k(\xi) = \xi k(1)$, because the surface area of a fractal pore is ξ times higher than that of a smooth pore of the same length and average pore cross-section.

The concentration profile in an open pore with the above boundary conditions is represented in Figure 3 and is given by:

$$\frac{C_A}{C_A^0} = \frac{\cosh\left[\Phi\left(1 - \frac{z}{L}\right)\right]}{\cosh\Phi \times \left[1 + \left(\frac{4D_K}{L\bar{u}}\right)\Phi \tanh\Phi\right]} \quad (6a).$$

Compared to the better known classical “reaction in an infinite slab” problem (Froment and Bischoff, 1990), with Dirichlet boundary conditions at the pore ends, an additional factor:

$$1 + \left(\frac{4D_K}{L\bar{u}}\right)\Phi \tanh\Phi \quad (6b),$$

appears in order to satisfy the concentration jump or the external mass transfer limitation at the pore ends.

This term becomes significant when the molecules diffuse through pores for which $\Phi > 1$ while L is not several orders of magnitude larger than the pore diameter, which may be the case in molecular simulations (see Section 3). The conversion of A in the pore is calculated by noting that the number of moles entering the pore per unit of area and per unit of time is given by $C_A^0 \bar{u} / 4$, while the net flux into

the pore is less as a result of the reaction in the pore, and is given by $-D_K \frac{dC_A}{dz} \Big|_{z=0^+}$, so that:

$$x_A = \frac{-D_K \frac{dC_A}{dz} \Big|_{z=0^+}}{\frac{C_A^0 \bar{u}}{4}} = \frac{1}{1 + \frac{L\bar{u} \coth\Phi}{4D_K\Phi}} \quad (7).$$

The effectiveness factor, finally, is the number of molecules which react in the pore, $x_A(C_A^0 \bar{u} / 4)$, divided by the total amount of molecules that would react in the absence of diffusion limitations:

$$\eta = \frac{\tanh\Phi / \Phi}{1 + \left(\frac{4D_K}{L\bar{u}}\right)\Phi \tanh\Phi} \quad (8).$$

Note that the same correction factor to the classical infinite slab result, Eq. (6b), appears.

Previous work already discusses how the fractal surface morphology, via Φ , has a very particular influence on diffusion-reaction processes in a pore, and consequently also in a complete catalyst particle, that cannot be reproduced by any model based on Euclidean geometry (Coppens and

Froment, 1995b, 1994). Differences between fractal and smooth cylindrical pores are enhanced when surface roughness also induces pore tortuosity so that the axial pore lengths are different for a given end-to-end distance. These formulas based on a continuum approach, however, do not explicitly reveal whether the self- or the transport diffusivity needs to be substituted into the result, and whether D_K is independent of the reaction rate coefficient, k . Dynamic Monte-Carlo simulations can shed more light on this.

3. Dynamic Monte-Carlo simulations

3.1 Methodology

The three-dimensional fractal pores used in the simulations have the same geometry as the model pores in our previous work on diffusion in the absence of reaction (Malek and Coppens, 2001, 2002). A typical pore segment is shown in Figure 1; its surface consists of statistically self-similar Koch surfaces that are generated recursively by transforming, using a predefined iteration rule, “wall tiles” of a smooth pore, in this case a pore with a square cross-section. This smooth pore is the 0-th generation, unperturbed pore. The iterative construction algorithm repeatedly replaces square tiles by a reduced copy of the generator. By applying this generator randomly, its indentation pointing either inside or outside the pore space with equal probability, the pore volume is preserved on average and a random fractal pore is generated. If the generator rule is always applied in the same direction, a deterministic fractal pore is formed. In the case of the generator shown in Figure 1(b), the smallest features decrease by a factor 3 in length after each generation, leading to pores like the one shown in Figure 1. The walls of a fractal pore consist of a large number of fractal tiles. The irregularity or roughness factor ξ of a pore at any generation n is given by the ratio of the pore surface area to the surface area of an unperturbed smooth pore with the same cross-section. For example, for the pore in Figure 1, $\xi = (13/9)^n$.

The simulation procedure to generate particle trajectories is an extension of the one used in our former study of diffusion in the absence of reaction [see Malek and Coppens (2002) for additional details]. Molecules are taken to be point masses, *i.e.*, molecular size effects are indirectly accounted for by performing simulations for a pore surface generation n that is still fully accessible by a molecule of size $\sim \delta_{max}/3^n$ (the smaller the molecule, the larger the level of detail and therefore the generation n that is accessible). All properties, like diffusivities and yields, are evaluated by ensemble averaging over various

molecular trajectories and, for random pores, over various realizations of the pore. A large number of simulations are performed, until convergence is obtained. When simulating Knudsen diffusion and first-order reaction, molecules do not interact with each other, so that only a single molecule needs to be considered at any time.

In the Knudsen diffusion regime, molecular trajectories are a chain of line segments connecting points on the pore wall, with the exception of the first and the last segment. Every trajectory is started by randomly choosing a position in the interior of the inlet cross-section. This initial position, plus a random direction, is assigned to a test molecule that moves through the entrance into the pore. When this molecule reaches the pore wall, it is assumed to undergo a diffuse reflection at the location of the molecule-pore wall collision, and new direction cosines are generated according to the cosine law. To record an impact, a Cartesian coordinate system (x, y, z) is built with the z -axis parallel to the direction of the pore axis. For the model pores considered here, all square surface tiles lie in equidistant planes parallel to $z = 0$, $x = 0$ or $y = 0$. Each plane consists of square units that either belong to the surface or not. A characteristic function for the pore is defined as follows:

$$Z(v) = \begin{cases} 1 & \text{if } v \text{ belongs to the pore surface} \\ 0 & \text{otherwise} \end{cases} \quad (9).$$

For a molecule moving through the pore space, a collision with the pore wall is determined by considering all potential collision points v along the current trajectory, for which $Z(v)=1$, and determining the shortest distance from the molecule's point of origin. The shortest distance leads to the physical collision point. If no reaction occurs (reactions are considered later), the molecule reflects from the wall in a diffuse way, *i.e.*, new direction cosines are randomly generated, and the procedure for locating the next molecule-wall collision is repeated.

Applying periodic boundary conditions on sufficiently long, representative segments of a pore – molecules leave the segment through one end and re-enter through the opposite end – allows saving computer memory for the representation of long pores. Only one such pore segment needs to be considered at any given time. Hence, a pore can be represented using moderate values of the number of fractal tiles, and extending the sample in the z -direction using periodic boundary conditions.

The self-diffusivity in the absence of reaction, D_K^s , is obtained from Einstein's relation:

$$D_K^s = \frac{|\mathbf{r}|^2 \bar{u}}{6l} \quad (10),$$

after calculating the end-to-end square displacement, $|\mathbf{r}|^2$, as well as the total trajectory length, l , after a large number of collisions, and ensemble averaging over a large number of molecules. Transport diffusion is simulated by imposing a concentration gradient over an open pore of finite length: When a molecule exits the real pore inlet or outlet, it does not re-enter through the other end, but periodic boundary conditions may be applied on parts of the pore. This corresponds to imposing a concentration C_A^0 at the inlet and a zero concentration at the outlet. To remove a bias due to pore entrance effects, transport diffusion is considered over the piece of pore stretching from the equilibration length until the other pore end, with respect to the concentration gradient ∇C_A over this piece. This equilibration length allows molecules to collide, on average, sufficiently frequently with the surface to remove any bias induced by infrequent collisions over a stretch shorter than a few cutoff lengths, $\delta_{\max}$ (Malek and Coppens, 2002). The transport diffusivity, D_K^t , is estimated from the transmission probability, f_t , *i.e.*, the fraction of equilibrated molecules (flux $N_{A,in}$) that leave the pore on the other side:

$$D_K^t = -\frac{f_t N_{A,in}}{\nabla C_A} \quad (11).$$

Diffusion and reaction in fractal pores of different roughness ξ and for different reaction rate coefficients k or k_s , is now simulated for the same conditions as in Section 2. A first-order catalytic reaction $A \rightarrow B$ is considered in open 3D pores of varying surface roughness (Figure 1). The pore length $2L = 1 \times 10^{-6}$ m and the pore diameter $d = 1 \times 10^{-8}$ m = $2L/100$. The concentration of the diffusing reactant A in compartments on both pore ends ($z=0$ and $z=2L$) is maintained at constant levels, C_A^0 , so that there is *no imposed concentration gradient* over the pore. The dynamic Monte-Carlo simulation procedure only differs from the procedure for pure Knudsen diffusion described earlier in that a collision with the wall may now lead to a reaction, according to a certain reaction probability p . A reaction occurs if a number p_r selected randomly between 0 and 1 is less than p . To investigate whether the self-diffusivity depends on k , eq. (10) is used, based on the trajectories of non-reacted molecules after a large number of collisions with the walls.

3.2 Simulation results and discussion

Results previously obtained for pure diffusion were already discussed in the introduction. In summary, $D_K^s(\xi)$ is roughness dependent, the values from dynamic Monte-Carlo simulations agreeing well with the analytical result, eq. (2), for any value of $\delta_{\max}$ up to the average pore diameter d , while D_K^t does not depend on roughness (Malek and Coppens, 2001). Our simulations also confirm Santra and Sapoval's (1998) result that there is no appreciable roughness dependence when the largest irregular surface indentations are still small compared to the pore diameter ($\delta_{\max} \ll d$). Catalyst characterization experiments however show that this geometric requirement is not met for many industrial nanoporous sorbents and catalyst supports, where the fractal perturbations may reach up to the size of the local channel diameter, *i.e.*, $\delta_{\max} \sim d$, in particular for sol-gel synthesized materials where pores are interstices between primary, rough aggregates (Coppens, 2001). Just like we did for pure diffusion, we therefore investigate the impact of surface roughness on diffusion limitations in catalysis for cases where surface roughness is appreciable, such as in the model pores discussed earlier. It should be stressed that possible effects of roughness and lateral molecular interactions on the *intrinsic* kinetics are ignored; such microscopic (quantum) effects may be significant and add on to the mesoscopic diffusion induced effects studied here (Somorjai, 1994; Neurock, Pallasana, and van Santen, 2000).

One of the prime objectives of the dynamic Monte-Carlo simulations is to compare the simulation results with those of the continuum model in the previous section for pores of different roughness ξ and a given value of the intrinsic reaction rate coefficient. When comparing pores of different roughness and the same average diameter d , the reaction rate coefficient is taken constant either per unit surface area ($k_s = \text{cst.}$) or per unit catalyst mass ($k = \text{cst.}$). The first case serves as a model for, *e.g.*, acid catalysis, while the second is realistic for, *e.g.*, supported metal catalysts where the metal loading is assumed to be the same, which, in effect, decreases the average k_s by a factor of ξ because the number of active sites remains the same yet the surface area of the support increases. Averaging out the activity over the pore surface can be done for long enough pores containing enough sites. Important in this regard is also to investigate how the accessibility and hence also the reaction probability is distributed over the surface. For a molecule diffusing through a deterministic fractal pore, in which the surface is constructed using a deterministic Koch surface generator, the square segments of the fractal tiles are not

equally accessible. Segments that are directly accessible from the pore space are hit more frequently than more hidden segments. This non-uniformity in the accessibility distribution of the surface largely disappears when a random Koch surface generator is used, so that the surface effectiveness factor $\eta^s \sim 1$.

From the total number of reactant molecules, M , entering the pore, some leave the pore through either end without reacting, while some react on the surface. For different values of the reaction probability p , the conversion x_A is readily calculated as the ratio of the number of reacting molecules in the pore to the total number of molecules A entering the pore, M . This ratio corresponds to the formulation in eq. (7), since the net inlet flux (denominator) equals the number of reacting molecules per unit cross-sectional area. In order to compare the Monte-Carlo results with the continuum model, the relation between the reaction rate constant, k , and the reaction probability, p , is needed:

$$k = k_s a_A = \left(\frac{p\bar{u}}{4} \right) a_A(\xi) = \left(\frac{p\bar{u}}{4} \right) \xi a_0 \quad (12)$$

(Somorjai, 1994), in which $a_A(\xi)$ is the specific area accessible to molecules A when the pores are of roughness ξ , and $a_0 = a_A(\xi=1)$ is the specific area of a porous material with smooth pores of the same average length and diameter as the rough pores.

Figure 4 shows the conversion x_A as a function of the reaction probability p for a smooth pore ($\xi=1$) and for a rough one with walls that are first- ($\xi=13/9$) or second-generation [$\xi=(13/9)^2$] random Koch tiles. Increasing the roughness increases the total surface area accessible to a reactant molecule, so that the number of collisions typically increases per unit pore length. This, in turn, increases the probability for a molecule to react within the pore if k_s is constant (same p), which leads to an increased conversion in rougher pores. Comparing rough and smooth pores with the same value of the reaction rate constant per unit catalyst mass, $k=k_s a_A$, shows that even here the conversion in rough pores differs from that in a smooth pore. Since it was shown earlier that the surface effectiveness factor η^s is the same, this is solely due to differences in diffusion limitations. Knowing that the transport diffusivity, D_K^t , does not depend on roughness, while the self-diffusivity, D_K^s , does, this is an indication that the self-diffusivity plays a determining role.

A clear way to show this is by calculating the Thiele modulus Φ , using eq. (5), and plotting the effectiveness factor η as a function of Φ . The effectiveness factor η is calculated from the ratio of the

number of reacted molecules to the number of molecules that would react in the absence of diffusion limitations. For M molecules entering a pore of length $2L$, it is easily shown that the maximum number of reacting molecules is $\min\{M, 2pM\xi a_0\rho_s L\}$.

For a given value of k , the Thiele modulus only depends on roughness if the self-diffusivity, eq. (2), is substituted for D_K in eq. (5). Figure 5 shows the results for a smooth pore (where self- and transport diffusivity coincide) and Figure 6 for a rough pore with $\xi=(13/9)^2$. The full lines in Figures 4, 5 and 6 correspond to the predictions of the continuum model [eqs. (7) and (8)], using eq. (5) for the self-diffusivity, D_K^s , which was shown earlier to correspond well with the Monte-Carlo simulations. The agreement between Monte-Carlo simulations and the continuum model predictions is excellent in all cases. Only for very strong diffusion limitations on the pore scale (high Φ) is there some deviation, which is to be expected as reactions are near instantaneous in this case, occurring after only a few collisions, so that a continuum description breaks down. The dotted line in Figure 5 corresponds to the classical relation for the effectiveness factor, $\tanh(\Phi)/\Phi$, without the correction for concentration jumps at the pore ends, eq. (6b). The results in Figure 6 again show excellent agreement between the “experimental” effectiveness factors found from dynamic Monte-Carlo simulations and those predicted by the continuum model based eq. (8), as long as the self-diffusivity, D_K^s , is substituted into this equation. Note that no fitting parameter was used. The results clearly deviate both from the predictions for a smooth pore (dashed line) and from those predicted by substituting for D_K the roughness independent transport diffusivity, D_K^t (dotted line).

This demonstrates the possibility to apply a continuum model to describe diffusion and reaction in (fractal) pores, and, by extension, in porous media with a fractal internal surface, but it also reveals that the catalyst morphology dependent self-diffusivity is the fundamental diffusivity to describe diffusion limited processes in catalysis. From a statistical point of view, this is not surprising: what matters is the frequency of collisions of individual molecules with the catalyst surface, and the trajectory followed by these molecules until they react or leave the pore. These phenomena are characterized by the self-diffusivity. The transport diffusivity describes the flow through the pore under the influence of an imposed concentration gradient, which in this case is zero. Looking at the continuum model equations, the result may perhaps be less expected, because of the flux relationship:

$$N_A = -D_K \nabla C_A \quad (13)$$

that is substituted into the continuity equation for the component A:

$$\nabla \cdot N_A = -\rho_s k C_A \quad (14)$$

to obtain eq. (4). Let us recall that for smooth pores, the difference between self- and transport diffusivity does not exist, so that the question which diffusivity to substitute into eq. (13), eq. (4) or eq. (5) does not raise itself. For a rough pore, it is essential to analyze what eq. (13) really means in the context of catalysis, in this case of a first-order reaction in a pore, in the Knudsen diffusion regime. Since there is no imposed concentration gradient, D_K simply cannot be the transport diffusivity. What it represents is the *tracer* diffusivity of molecules A. The molecules injected into the pore can indeed be viewed as tracers, since they do not directly interact with any other molecules A (or B). They may react when colliding with the surface and are, in doing so, transformed into isomer molecules B. The fluxes of species A and B are identical and opposite (equimolar counterdiffusion), so that their sum is zero: there is no net flux of A+B. Furthermore, it is known from non-equilibrium statistical mechanics that the tracer diffusivity and self-diffusivity of non-interacting particles are identical (see, *e.g.*, the fluctuation-dissipation theorem or Kärger and Ruthven, 1992). This explains why the tracer diffusivity in eq. (13) may be replaced by the self-diffusivity. These results lead us to conclude that the self-diffusivity is the fundamental diffusivity in catalysis, at least in the description of a first-order reaction in the Knudsen regime.

Also in zeolites, self- and tracer diffusivity coincide, while the transport diffusivity differs at non-zero occupancies (Kärger and Ruthven, 1992; Keil, Krishna and Coppens, 2000). Also here, the difference is due to trapping (Malek and Coppens, 2001; 2002). Based on the observation that our results and arguments do not specifically depend on the *origin* of the difference between self- and transport diffusivity, which in the case studied here is fractal surface roughness, we therefore postulate that our results may be more generally applicable, *i.e.*, that self-diffusivities are the fundamental diffusivities in catalysis. This implies that also in other situations where self- and transport diffusivity differ such as in zeolites, it is the self-diffusivities that should be used in describing diffusion limited reactions in catalyst particles. Work to investigate this generalization to other situations, such as diffusion and reaction in zeolites, is underway.

4. Conclusions

Dynamic Monte-Carlo simulations of diffusion limited reactions in rough, fractal pores, show the significant effect of surface roughness on the conversion and the effectiveness factor. A continuum description is appropriate for all but situations where the diffusion limitations are extremely severe, so that the reaction is virtually instantaneous. Furthermore, it is the morphology dependent self-diffusivity and not the morphology independent transport diffusivity that is the relevant transport property in catalysis.

Notation

a_0	specific surface area in a porous medium with smooth walls ($\text{m}^2/\text{kg}_{\text{cat}}$)
a_A	specific surface area accessible to species A ($\text{m}^2/\text{kg}_{\text{cat}}$)
A	reacting species in first-order reaction
B	product species in first-order reaction
C_A	concentration of component A in the pore (mol/m^3)
C_A^0	concentration of component A at the pore ends (mol/m^3)
D_{ads}	fractal (adsorption) dimension of the surface
D_K	Knudsen diffusion coefficient for component A (m^2/s)
D_{K0}	Knudsen diffusion coefficient for a pore with smooth walls (m^2/s)
D_K^s	Knudsen self-diffusivity (m^2/s)
D_K^t	Knudsen transport diffusivity (m^2/s)
d	effective pore diameter (m)
f_t	transmission probability
k	rate constant of first-order reaction ($\text{m}^3/\text{kg}_{\text{cat}} \text{ s}$)
k_s	rate constant of first-order reaction ($\text{m}^3/\text{m}_{\text{cat}}^2 \text{ s}$)
l	total trajectory length of a molecule (m)
L	pore length (m)

M	number of molecules entering the pore
N_A	molar flux of species A (mol/m ² s)
p	reaction probability upon collision with the pore wall
p_0	return probability
$\bar{u}$	average molecular velocity (m/s)
x_A	conversion of A
$Z(\mathbf{v})$	characteristic function of the medium as a function of the position vector
$z_{\max}$	axial pore length (m)

Greek letters

α	geometry dependent parameter in equation 2
β	geometry dependent parameter in equation 2
δ	molecular diameter (m)
$\delta_{\max}$	outer cut off of the fractal scaling regime (m)
δ'_A	normalized effective diameter of molecule A of size δ (m)
η^s	surface effectiveness factor for a reaction, reflecting a nonuniform accessibility distribution over the surface
η	pore effectiveness factor
ρ_s	catalyst density (kg/m ³)
Φ	Thiele modulus of the pore
ξ	pore roughness factor
Ω	pore cross-sectional surface area (m ²)

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Figure captions

Figure 1. (a) Self-diffusivity (circles) and transport diffusivity (squares) in the Knudsen regime as a function of the roughness factor $\xi=(13/9)^n$ for a fractal pore with tiles that are n -th generation random Koch surfaces. Results are normalized with respect to D_{K0} , which is the Knudsen diffusivity in a smooth pore ($n=0$). The insert shows a segment of a second-generation pore ($n=2$). (b) A random 3D Koch surface generator.

Figure 2. Segment of a fractal pore with axial length $z_{\max}=2L$ and zero concentration gradient over the pore.

Figure 3. Concentration profile of component A, reacting according to a first-order reaction with $\Phi = 3.88$, in an open pore of length $2L$.

Figure 4. Conversion (x_A) calculated by dynamic MC simulations as a function of reaction probability (p) for a first order reaction in smooth ($\xi=1$: circles) and rough pores: ($\xi=13/9$: diamonds; $\xi=(13/9)^2$: triangles). The full line corresponds to analytical calculations in which the self-diffusivity is used.

Figure 5. Pore effectiveness factor as a function of Thiele modulus for a first order reaction in a smooth pore, calculated by MC (points) and analytically (full lines). The dotted line corresponds to the common classical prediction, $\eta=\tanh(\Phi)/\Phi$. Insert shows the graph in log-log scale.

Figure 6. Pore effectiveness factor as a function of Thiele modulus for a first order reaction in a fractal pore with walls that are second-generation Koch surfaces ($\xi=(13/9)^2$). The full line corresponds to analytical calculations where the self-diffusivity is used, while the dotted line corresponds to analytical calculations where the transport diffusivity is used. The dashed line represents the results for a smooth pore. Insert shows the graph in log-log scale.