PHYSICAL REVIEW E VOLUME 55, NUMBER 1 JANUARY 1997

Diffusion and reaction in percolating pore networks

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(Received 12 April 1996)

We address the problem of diffusion and reaction in porous catalysts subjected to percolation disorder. The results with an idealized pore network indicate that the fractal characteristics of the void space can have a remarkable influence on the transport and reactive properties of the system. Within a specific range of length scales, we observe scaling behavior relating the catalytic effectiveness of the network and the diffusion-reaction ratio $\overline{J_N} \propto (D/K)^{1/d_R}$. In addition, the exponent d_R is consistently in the range $d_w < d_R < d_w'$, where d_w is the two-dimensional random walk exponent on the incipient infinite cluster and d_w' is the corresponding diffusion exponent which includes *all* clusters of the system at the percolation threshold. Moreover, in contrast with diffusion under ''inert'' conditions, where the ''dangling'' bonds in the percolating cluster do not play any role in transport, these elements become active zones due to the reaction mechanism. We also outline some specific guidelines to demonstrate the relevance of these results in the context of design and characterization problems in heterogeneous catalysis. [S1063-651X(97)10801-7]

PACS number(s): 47.55.Mh, 05.40.+j

I. INTRODUCTION

The development of modeling techniques for the description of transport phenomena through the interstitial void space of disordered porous catalysts represents a genuine challenge, due to inherent limitations of traditional models which cannot explicitly account for topological and morphological characteristics of real porous media [1]. The classical approach to model diffusion and reaction in porous catalysts is to consider the catalyst particle as a homogeneous system where reagents and products can freely diffuse and react according to a given effective transport coefficient and an intrinsic reaction mechanism. Under steady-state conditions, this situation can be mathematically formulated as

$$D_{\mathrm{eff}} \nabla^2 C + R = 0, \tag{1}$$

where C is the concentration of the reacting species within the catalyst, D_{eff} its effective diffusivity, and R represents the intrinsic kinetics, expressing the local rate of creation or annihilation per unit volume of the species one desires to trace in the system.

Recently, it became clear that the classical diffusion formalism, which is valid for Euclidean geometries, cannot be used to provide a macroscopic description of transport phenomena in many disordered materials. In the case of porous media, the breakdown of this conventional transport theory can be clearly understood as a consequence of the intrinsic structural heterogeneity of the complex void space geometry, causing significant modifications in the diffusional characteristics of the system. Generally speaking, the departure from the classical behavior usually occurs in the form of a subdiffusive regime which has been extensively investigated [1–4]. The mathematical concept of fractals and the use of percolation models as an idealized description for disordered media turned out to be fundamental ingredients to analyze and predict theoretical properties of anomalously diffusive systems of transport [3,5–10]. There are a number of experimental works showing strong evidence that, within some limited range of length scales, many porous catalysts can be considered as realizations of fractal morphologies [11]. Much less effort has been dedicated to the study of diffusion and reaction in fractal geometries, and its consequences on the reactive properties of porous catalysts [12–16]. However, it is not easy to transpose and systematically apply fractal concepts in order to solve problems in catalysis.

An important issue in the design of most catalytic reactors is the choice of the size of the catalyst pellet. Diffusion is normally considered to be a deleterious mechanism because it might restrict the transport of reagent into the deepest regions of the pellet, reducing the overall reactivity of the available active surface area. Under these circumstances, the smallest pellet would be the preferred material. On the other hand, it is well known that small particles produce ''tight'' packings, which require a large consumption of energy to pump the reacting species through the extraparticle void space in a fixed bed reactor. Thus, there is an important trade-off between catalyst efficiency and energy consumption. The problem could be better analyzed if we had a more realistic model for the structure and phenomenology of the diffusion-reaction system, but few attempts have been made to develop a coherent framework where this problem could be properly examined. Sahimi applied the network of pores model to simulate the effectiveness of an idealized catalyst under different diffusion-reaction conditions [17]. The results with a disordered and fully occupied lattice show a marked contrast when compared with the classical description, but no reference is made relating the structural features of the pore space and its transport properties.

Just above the critical point, the incipient infinite percolation cluster is an example of a random fractal that can be used as a conceptual model for real pore catalysts (Fig. 1).

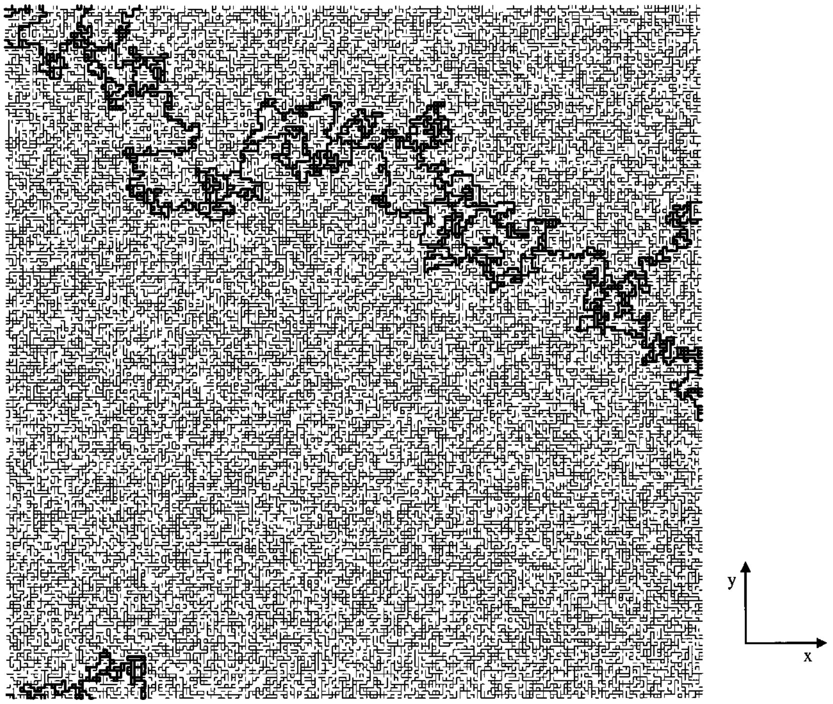

FIG. 1. Typical realization of a 200×200 percolating square network at the threshold probability ($p = p_c$). The thick lines correspond to the conducting backbone available for electrical transport in the system. Periodic boundary conditions are imposed in the transverse direction (y direction).

One advantage of using the percolating structure as a model of porous media is the large amount of research work performed to characterize such morphology, and a comprehensive set of precisely calculated critical exponents is available to describe its fractal features. Our main objective here is to investigate the effects of structural self-similarity upon the catalytic effectiveness of percolating pore networks. We show by computational simulation that, within some range of diffusion reaction conditions, the fractal aspect of the porous structure can strongly influence the global effectiveness of the reacting system. This might have profound implications on the design strategy currently applied for the project of real catalytic reactors in important technological processes.

II. MODEL

Based on the general framework of bond percolation disorder, we develop a practical model to study the influence of the void space on the catalytic characteristics of the system. We represent the structure of the porous catalyst by a two-dimensional square network of size L, where cylindrical pores of constant length and radius r are connected to sites of negligible volume. Each cylinder is open with a probability p and blocked with a probability $1-p$.

We assume that the inner surface of every open pore has a homogeneous distribution of active sites, at which a first-order reaction ($A \rightarrow B$) can take place in the presence of reagent species A. Also, if the reactant and product molecules are considerably smaller than the capillary radius r, a continuum description for diffusion and reaction can be adopted at the mesoscopic pore level. The concentration profile $c(x)$ of the reactive tracer A diffusing inside a typical open pore joining adjacent nodes i and j satisfies the mass conservation equation

$$D\frac{d^2c}{dx^2} = Kc, \tag{2}$$

where x is the axial coordinate in the pore, D the molecular diffusion coefficient, and K the intrinsic reaction rate constant. The boundary conditions are

$$c(0) = c_i \quad \text{and} \quad c(l) = c_j . \tag{3}$$

The molar flux of the tracer into a pore is,

$$J_{ij} = -\pi r^2 D \left(\left. \frac{dc}{dx} \right|_{x=0} \right)_{ij} . \tag{4}$$

From the solution of Eqs. (2) and (3), J_{ij} can be expressed as a linear function of the two concentrations at the connected nodal points [17,18]

$$J_{ij} = \pi r^2 (KD)^{1/2} \left[\frac{c_i}{\tanh(\beta l)} - \frac{c_j}{\sinh(\beta l)} \right], \tag{5}$$

where $\beta \equiv (K/D)^{1/2}$.

Considering the sites to be perfect mixing points with no reaction or tracer accumulation, we find the following identity for the mass conservation at each internal site:

$$\sum_{j=1}^{\delta} J_{ij} = 0, \tag{6}$$

where the sum runs over the δ nodes $j = 1, \ldots, \delta$ connected to node i in the capillary maze. We also impose a fixed concentration C_0 at the entrance of the inlet pores, periodic boundary conditions in the transverse direction of the lattice (y direction in Fig. 1) and gradientless boundary conditions at the exit of the outlet pores. Hence, the mass balance for all internal nodes can be expressed in matrix form as

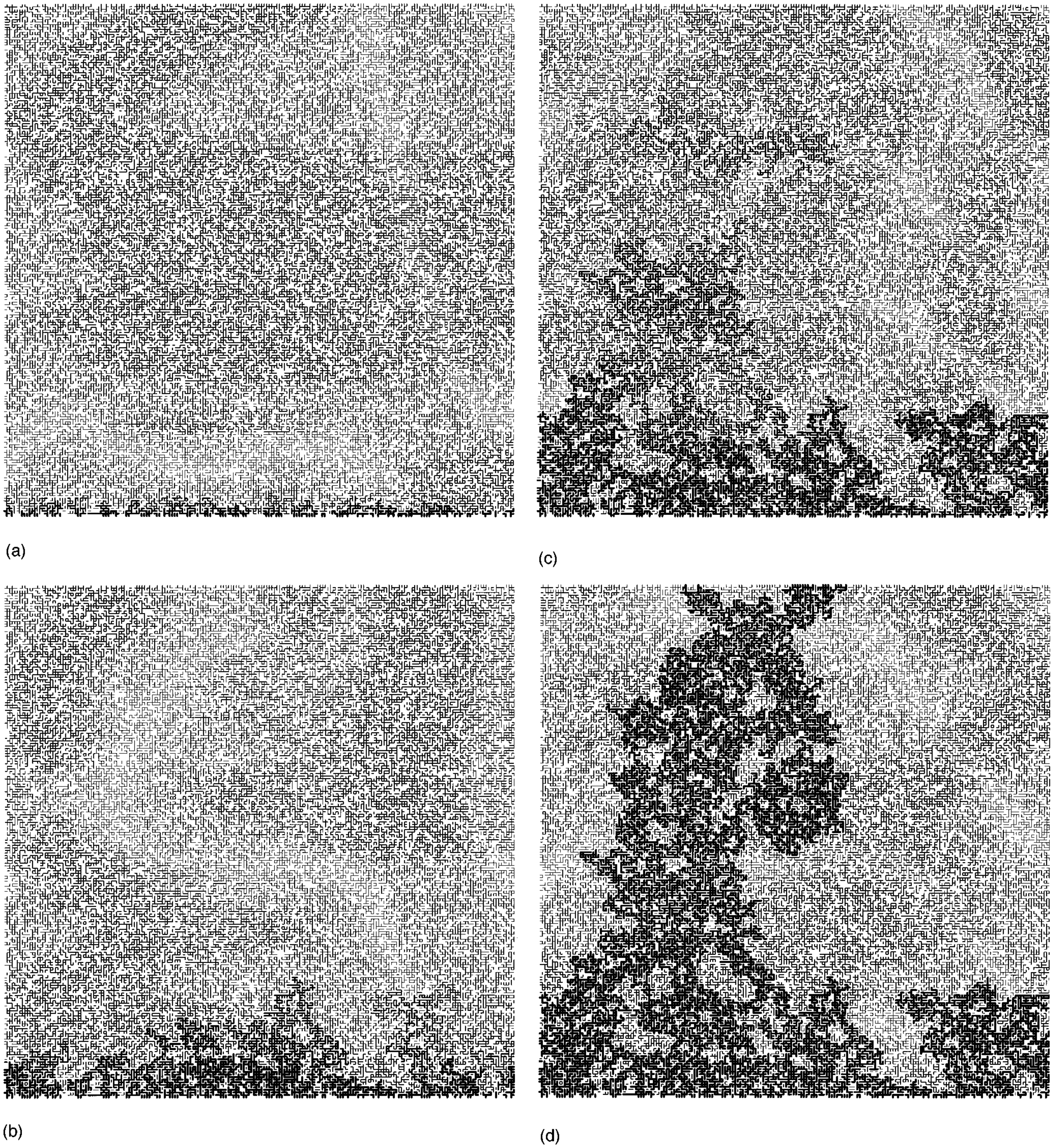

FIG. 2. Mass flux fields in a typical realization of a 200×200 percolating square network subjected to various diffusion-reaction conditions parametrized by $\alpha \equiv D/K$: (a) $\alpha = 10^2$, (b) $\alpha = 10^4$, (c) $\alpha = 10^6$, and (d) $\alpha = 10^8$. The thickness of the bonds corresponds to the magnitude of the mass flux of reactant through them.

$$\mathbf{A} \cdot \mathbf{c} = \mathbf{b}. \tag{7}$$

Here **A** is a matrix of conductance coefficients, **c** a vector of nodal concentrations, and **b** an input vector corresponding to the network boundary conditions. We used a standard subroutine for sparse matrices to solve the system of linear algebraic Eq. (7) for the nodal concentrations.

III. RESULTS

Before relating any transport property of the system with its fractal characteristics in a quantitative way, it is instructive to visualize the effect of increasing the diffusion-reaction ratio $\alpha \equiv D/K (= 1/\beta^2)$ on the transport of reactant inside a typical pore volume. Figures 2(a)–2(d) have been generated from the solution of Eq. (7) for a single random realization of the network at $p = p_c$, plotting all bonds in the percolating structure and assigning their thickness in accord with the mass flux J_{ij} through the respective cylindrical tube in the capillary model.

At low values of α, the reactant either diffuses very slowly into the catalyst pore space, or it is rapidly consumed by reaction at the active surface area of the capillaries. As a consequence, the mass flux of the reacting tracer is entirely confined to the entrance pores of the lattice [Fig. 2(a)]. As we gradually increase α, the tracer molecules can penetrate deeper into the pore space [Figs. 2(b) and 2(c)]. In the absence of diffusional limitations to mass transfer, or at very large values of α [Fig. 2(d)], the localized flux through all accessible pores in the lattice should be the same, and equal to a maximum value

$$J_{ij}^{\max}=\pi r^2 lKC_0. \tag{8}$$

Under these conditions, we can readily identify the regions in the network where transport and reaction are allowed to occur.

It is interesting to note that, unlike the problem of electrical transport in percolating resistor networks, the ‘‘dangling zones’’ [3] are an active part of the incipient ‘‘infinite’’ cluster, i.e., the large cluster which ‘‘spans’’ from one side to another in the x direction of the lattice. Apart from the spanning cluster, the clusters in direct contact with the inlet side of the network are also accessible to tracer diffusion and reaction.

The active role played by the dangling zones under diffusion-reaction conditions provides a plausible explanation for the following unsolved question in the field of heterogeneous catalysis. There is a substantial amount of experimental research showing strong evidence that the macroscopic measure of the diffusion coefficient in some catalysts under inert conditions can be significantly different from the ‘‘reactive’’ value of this transport parameter [19–21]. From the simulations presented here, we could simply argue that this discrepancy is due to the dramatic change in the active volume when switching from reactive to inert conditions. Correspondingly, the diffusivity in the absence of reaction would be equivalent to the conductivity in a resistor network analog, where the dangling bonds behave as stagnant zones with no current passing through them. This contrast can be easily seen in Fig. 3, where the active bonds from one reactive realization of the system with no diffusional limitation [large α, see Fig. 2(d)] have been plotted together with the ‘‘conducting backbone’’ of the corresponding percolating resistor network.

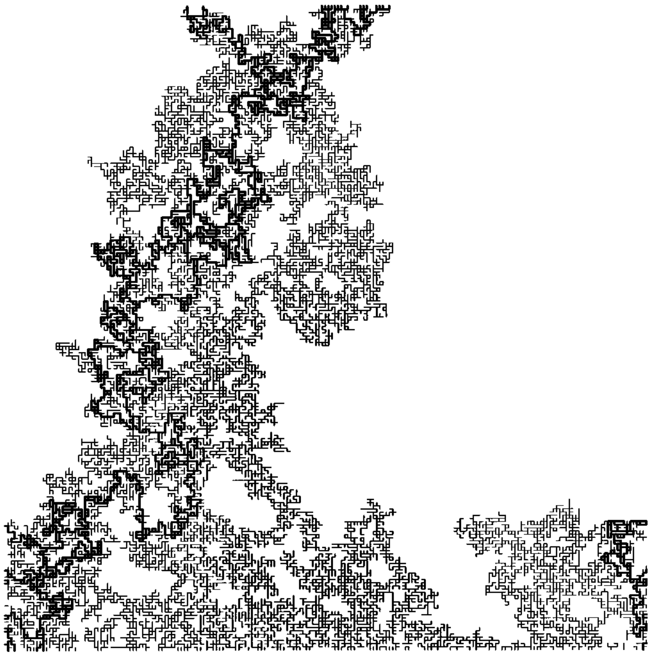

FIG. 3. Plot of the conducting backbone (thick lines) and the active bonds available for diffusion and reaction (thin lines) in a typical realization of a percolating network.

The implications of these facts on the scaling behavior of the system can be quantitatively analyzed. From the solution of Eq. (7) for different values of α, we can calculate the total molar flux J_N penetrating a given realization of the network pore volume. In order to measure how much the reaction rate is decreased by diffusional resistances, it is practical to define a quantity usually called the ‘‘effectiveness factor’’ of the pore catalyst [17],

$$\overline{J_N}\equiv\frac{J_N}{J_R}, \tag{9}$$

where J_R is the molar flux due to reaction without diffusional limitations. In particular, for a first-order reaction,

$$J_R=N_a\pi r^2 lKC_0, \tag{10}$$

where N_a is the total number of accessible pores in the network.

We performed simulations comprising 100 realizations of 200×200 networks at the percolation threshold, $p=p_c$. Figure 4 is a double logarithmic plot of the average J_N values against the parameter ratio α. At very low values of α, the concentration of reactant drops rapidly, and approaches zero at the entrance pores of the structure. In this situation of

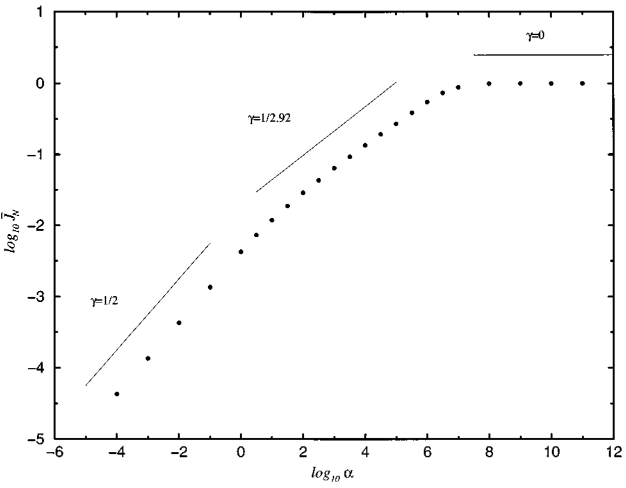

FIG. 4. Double-log plot of $\overline{J_N}$ as a function of the diffusion-reaction ratio $\alpha\equiv D/K$. The error bars are smaller in size than the symbols. Straight lines showing the expected limiting, and scaling behaviors, are also plotted for reference.

strong pore resistance, we expect to recover the classical behavior for diffusion and reaction in a single pore [14],

$$\overline{J_N} \propto \alpha^{1/2} \equiv \lambda, \tag{11}$$

where we interpret the ratio $\alpha^{1/2}$ as a penetration length, λ.

At very large values of α, diffusion offers negligible resistance to reaction, and the penetrating molar flux should be constant and equal to a factor times the total accessible volume of the pore network. This is the point where the reactant species can have free access to the active surface of all pores in the percolating cluster, a situation which is equivalent to stating that the catalytic effectiveness of the system is maximum or equal to 1,

$$\overline{J_N} = 1. \tag{12}$$

At intermediate values of α, however, a typical scaling behavior can be observed, which persists for more than four orders of magnitude. In this range of α values, the reactive tracer experiences the fractal structure of the available pores in the network. We would then expect the mass transport through the porous media to follow an anomalous diffusion behavior. The penetration length λ in this regime should scale as

$$\lambda \propto (Dt)^{1/d_R}, \tag{13}$$

where d_R is the critical exponent for diffusion and reaction in the percolating structure. In addition, if we make use of the relations $\overline{J_N} \propto \lambda$ and $K \propto t^{-1}$, the scaling ansatz Eq. (13) can also be expressed in a time independent way as

$$\overline{J_N} \propto \alpha^{1/d_R}, \tag{14}$$

which is more appropriate for the description of our particular system.

The accessible volume for diffusion and reaction involves not only the incipient infinite cluster but also the smaller clusters attached to the open side of the lattice. Accordingly, the critical exponent d_R should be taken as an intermediate value between the two-dimensional random walk exponent on the incipient cluster ($d_w \approx 2.87$) and the corresponding diffusion exponent which includes all clusters of the system at the percolation threshold ($d_w' \approx 3.02$) [2]. Indeed, this is consistent with the results shown in Fig. 4, where the logarithmic variation of the normalized flux penetrating the network in the diffusion-reaction range of $1 < \alpha < 10^5$ closely follows a straight line with slope $\gamma = 1/d_w'$. These limits for α can be directly related to the particular minimum length scale and system size adopted in this study. Therefore, the smaller limit should correspond to the square of the lower cutoff size of the system ($l^2 = 1$), and the larger limit should be comparable to the square of the network size used in the simulations ($L^2 = 4 \times 10^4$). Both are in perfect agreement with our simulations.

Finally, it is interesting to compare the results shown in Fig. 4 for percolating pore networks at the critical point ($p = p_c$) with the behavior of a fully occupied lattice ($p = 1$). As shown in Fig. 5, this can be done if we plot the normalized flux for both systems against the rescaled diffusion-reaction parameter,

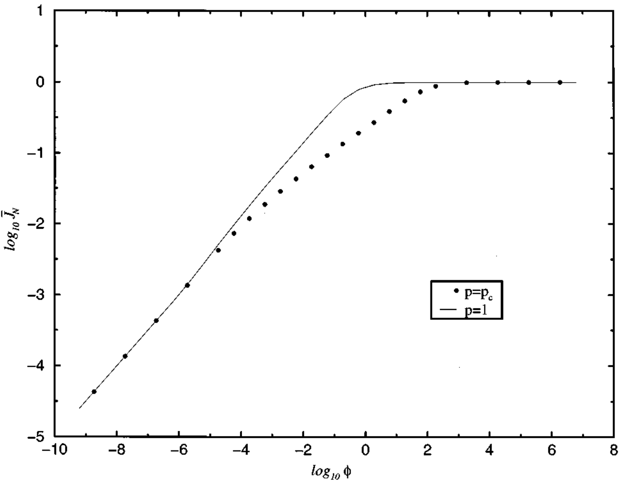

FIG. 5. Double-log plot of $\overline{J_N}$ as a function of the rescaled variable ϕ. The solid line corresponds to the fully occupied lattice ($p = 1$), and the circles to the average values obtained from simulations with percolating networks ($p = p_c$).

$$\phi = \alpha \left(\frac{N_i}{N_a l} \right)^2, \tag{15}$$

where N_i is the number of accessible pores at the network inlet. Expectedly, in the limiting situations of strong (low ϕ) and negligible (high ϕ) diffusional resistances, the two systems should follow exactly the same behavior which is independent of the structural features of the network. However, in the limited range of ϕ values where the fractal geometry of the percolating structure has a marked influence on its diffusive characteristics, a large discrepancy can be observed between the effectiveness of both idealized catalysts.

IV. DISCUSSION

We developed a model that is capable of describing diffusive mass transport and chemical reaction in percolating pore structures. The results from steady-state simulations reveal the strong influence of the pore fractality on the global effectiveness of the diffusion-reaction system. This represents a clear indication that one must characterize the possible self-similar morphology of the catalyst porous matrix in order to understand its behavior under reactive conditions. In this way, we believe that the modeling technique utilized here can provide some interesting guidelines for the design problem of a suitable catalyst porous structure for a given reactive system. For example, our results clearly show that, in the scaling range of the diffusion-reaction parameter α, the effectiveness of the pore catalyst can be largely overestimated if the self-similar aspect of the void space is not taken into consideration. Another result of potential interest from our simulations is the remarkable difference we found between the effective volumes for transport in the pore network under inert and reactive conditions. We believe that this might be intimately related with the divergence previously reported in several experiments to measure effective diffusion coefficients. In conclusion, the present modeling approach is flexible to represent more specific morphological and topological characteristics of the pore space and can also be applied to other phenomena occurring with diffusion through a porous medium.

ACKNOWLEDGMENTS

We thank Showa Denko K. K. and the NSF for support, and A. Scala, F. W. Tavares, H. Makse, and L. da Silva for helpful discussions.

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