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Scaling behavior of diffusion and reaction processes in percolating porous media

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We investigate the diffusion-reaction behavior of two-dimensional pore networks at the critical percolation point. Our results indicate the existence of three distinct regimes of reactivity, determined by parameter $\xi \equiv D/(Kl^2)$, where D is the molecular diffusivity of the reagent, K is its chemical reaction coefficient, and l is the length scale of the pore. First, when the diffusion transport is strongly limited by chemical reaction (i.e., $D \ll K$), we recover the classical scaling behavior $\Phi \sim L\xi^{1/2}$, where Φ is the mass flux of reagent penetrating the pore space and L is the system size. Second, at an intermediate range of ξ values, when the process is influenced by the fractal morphology of the percolation cluster, we observe an anomalous diffusion scaling, $\Phi \sim L^{\alpha/2}\xi^{\beta}$, with an exponent $\beta \approx 0.34$. Third, in the absence of diffusional limitation ($D \gg K$), the flux of reagent reaches a saturation limit Φ_{sat} that scales with the system size as $\Phi_{\text{sat}} \sim L^{\alpha}$, with an exponent $\alpha \approx 1.89$, corresponding to the fractal dimension of the sample-spanning cluster. We then show that the variation of flux Φ calculated for different network sizes at the second and third regimes can be adequately described in terms of the scaling relation, $\Phi \sim L^{\alpha} f(\xi/L^{z})$, where the crossover exponent $z \approx 2.69$ is consistent with the predicted scaling law $\alpha = 2\beta z$.

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I. INTRODUCTION

Due to its broad technological applications, heterogeneous catalysis has been the subject of extensive research in many fields of chemistry, engineering, and physics [1–3]. In particular, the development of models for the description of diffusion and reaction in disordered media represents an important step for the design of real porous catalysts. For instance, the size of the catalyst pellet is frequently used as a design parameter for packed bed reactors when diffusional limitations to mass transport restrict the free access of reagent species into the deepest regions of the porous substrate. This is a typical situation where diffusion appears as an undesirable mechanism since it can significantly reduce the reactivity of the available catalytic surface area. From this point of view, small pellets would be the preferred filling material for a fixed bed reactor, if the packings resulting from their assemblage were not so "tight," requiring a large consumption of energy to pump the reacting species through the extra-particle void space. Certainly, this important trade-off between catalyst efficiency and energy consumption has to be carefully investigated within the framework of realistic models for the diffusion-reaction system.

There are two essential aspects for the comprehension of physical processes in porous catalysts: the structural and phenomenological aspects. The first is intimately associated with morphological characteristics of the interstitial pore space and the second makes reference to the transport mechanisms and physico-chemical interactions taking place at the pore level. The traditional approach to this problem is to assume the catalyst as a pseudohomogeneous medium and mathematically model the diffusion-reaction phenomenon under steady-state conditions as

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

where C is the concentration of reagent, D_{eff} is an effective diffusion coefficient, and R represents the intrinsic kinetics of the reaction mechanism, expressing the rate of creation or annihilation per unit volume of the reacting species. Although valid for most Euclidean geometries and homogeneous media, this classical diffusion formalism breaks down as a macroscopic description for transport phenomena in disordered materials with *heterogeneous geometry*. For example, anomalies in the form of a subdiffusive regime of transport through the complex structure of fractal materials have been observed in experiments and extensively investigated through numerical simulations [4,5]. Few studies, however, have been dedicated to the investigation of diffusion and reaction in fractal media, and its consequences on the reactive properties of porous catalysts [6–10].

Extrapolating the descriptive features of the pseudohomogeneous representation Eq. (1), capillary network models are based on a detailed description of structure and phenomenology and so can provide a more realistic interpretation for the diffusion-reaction phenomenon in porous catalysts [11–14]. In a previous study [15], this class of models has been used to investigate the problem of diffusion and reaction in porous catalysts subjected to percolation disorder. 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. The results from steady-state simulations revealed the strong influence of the pore fractality on the global effectiveness of the diffusion-reaction system. As a consequence of the scaling behavior observed within a specific range of diffusion-reaction conditions, it has been shown that the effectiveness of the pore catalyst can be largely overestimated if the self-similar aspect of the void space is not properly taken into consideration.

In the present study, we investigate the scaling properties of the catalytic effectiveness of two-dimensional percolating pore networks at criticality. We show through extensive numerical simulations that the finite-size scaling analysis of the percolating system is compatible with a scaling *ansatz* that accounts for the dependence of the effectiveness on the system size and diffusion-reaction conditions. This paper is organized as follows. In Sec. II, we present the mathematical model to simulate diffusion and reaction in percolating porous media. We show the results in Sec. III and Sec. IV comprises discussion and summary.

II. MODEL FORMULATION

We first describe the geometry of the disordered system studied here. Our basic model of a porous catalyst has its origins on a two-dimensional square lattice, from which a bond percolation cluster is extracted at criticality [5,16]. We assume that the inner surface of every open pore of constant length l and radius r has a homogeneous distribution of active sites, where a first-order reaction ($A \rightarrow B$) takes place. Also, if the reactant and product molecules are considerably smaller than the capillary radius r, a continuum description for diffusion and reaction is representative of the catalytic phenomenon at the 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 is the molecular diffusion coefficient, and K is the intrinsic reaction rate constant. The following boundary conditions are employed:

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

and the molar flux of the tracer into a pore is given by

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

From the solution of Eqs. (2) and (3), J_{ij} can be expressed as a linear function of the two concentrations at neighbor nodes,

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

where $\lambda \equiv (D/K)^{1/2}$. The molecular diffusion approximation used here can only be locally valid if the mean free path of the diffusing reactant is sufficiently smaller than the pore radius. The molecular mean free path constitutes a lower cutoff for the validity of our description. If the pore surface presents smaller geometrical features, it results in an equivalent intrinsic reactivity determined by the Knudsen regime of diffusion [9,17]. Considering the nodes to be perfect mixing points with no reaction or tracer accumulation, mass conservation gives

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

where the sum runs over the δ nodes $j=1, \ldots, \delta$ connected to node i in the capillary network. A fixed concentration C_0 at the entrance of the inlet pores is imposed along with periodic boundary conditions in the transverse direction of the lattice and gradientless boundary conditions at the exit of the outlet pores. The solution of the system of linear algebraic equations (6) subjected to these constraints is calculated in terms of the node concentration field by means of a standard subroutine for sparse matrices. Finally, we compute the total flux penetrating the system as

$$\Phi=\pi r^2(KD)^{1/2}\sum_{j=1}^{\delta}\left[\frac{C_0}{\tanh(l/\lambda)}-\frac{c_j}{\sinh(l/\lambda)}\right], \tag{7}$$

where the sum is over the nodes connected to the existing pores that constitute the inlet face of the network with constant concentration C_0.

III. RESULTS

We performed simulations with 3200, 1600, 800, 400, and 200 realizations of networks of size $L=32$, 64, 128, 256, and 512, respectively, generated at the critical point, $p=p_c$, and for a wide range of values of parameter $\xi \equiv D/(Kl^2)=(\lambda/l)^2$. For each realization, we compute flux Φ and average it over all samples. Figure 1 is a logarithmic plot showing the dependence on ξ of the average mass flux for different network sizes. For comparison, we also show the reactive behavior of a fully occupied lattice ($p=1$) of size $L=512$ for the same range of ξ values. Three distinct regimes of diffusion reaction can be clearly identified in the case of networks at criticality. First, a typical scaling region

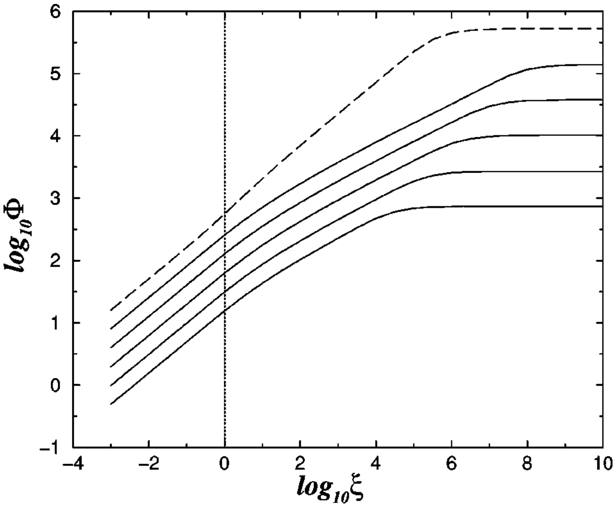

FIG. 1. Log-log plot of the reagent mass flux Φ penetrating the pore network versus the diffusion-reaction parameter ξ. From the bottom to the top, the solid lines correspond to critical percolation networks with sizes $L=32$, 64, 128, 256, and 512. For comparison, the dashed line is the result for a fully occupied network ($p=1$).

at low values of ξ crosses over to another power-law zone, but with a smaller exponent. The second scaling region extending over an intermediate range of ξ values eventually saturates to reach a maximum mass flux that strongly depends on the system size. In the case of the first scaling region, two equivalent situations can be representative of the diffusion-reaction phenomenon: either the reactant diffuses very slowly into the catalyst pore space, or it is rapidly consumed at the active surface area of the access capillaries. In one case or the other, since the reagent mass flux remains confined to the inlet pores of the lattice, we recover the classical scaling behavior for diffusion and reaction in a single smooth pore,

$$\Phi \sim L\xi^{1/2}, \tag{8}$$

where $\xi^{1/2}$ is a local measure of the diffusive penetration extent limited by chemical reaction. Factor L accounts for the fact that an average number of pL capillaries are accessible for diffusion and reaction at the network entrance, although some of these tubes might not belong to the sample-spanning cluster. To ensure the validity of our continuum approach at the pore level in terms of the molecular diffusion description Eq. (2), here we assume that the minimum value used for λ in all simulations, $\lambda_{min}=(\xi_{min})^{1/2}l\approx 0.03l$, is very large compared to the mean free path of the reagent species.

By gradually increasing ξ, the reagent species can penetrate deeper into the percolation porous media before being depleted at the surface of the pores. At very large values of ξ (i.e., in the absence of diffusional limitations), the reagent species have free access to the active surface of all pores in the percolating cluster. The mass flux reaches a saturation value Φ_{sat} that is strictly reactive and therefore proportional to the total accessible volume of the pore network. In particular, for a first-order reaction taking place in a percolation network at criticality, it follows that

$$\Phi_{\mathrm{sat}} \sim L^{\alpha}, \tag{9}$$

where $\alpha \approx 1.89$ is the fractal dimension of the sample-spanning cluster [5,16]. In Fig. 2 we show a log-log plot of the variation of Φ_{sat} on the system size L. The best linear fit to the data is quite consistent with the power-law behavior Eq. (9) and the resulting exponent $\alpha = 1.89 \pm 0.03$ is in excellent agreement with the expected value.

At intermediate values of ξ, all curves in Fig. 1 corresponding to networks at criticality (solid lines) display a crossover to a second scaling zone that starts at $\xi \approx 1$ and persists for more than four orders of magnitude. As shown in Fig. 3, this change is better visualized if we simply rescale flux Φ by factor pL. Apart from the collapse of the profiles at the initial scaling region, this transformation also reveals a typical finite-size effect at the second scaling zone that is reminiscent of the dynamical roughening observed in some surface growth models [18]. In this region of ξ values, the reagent species experiences the fractal structure of the sample-spanning cluster. As a consequence, we can identify a well-defined region where the penetrating flux follows the scaling form

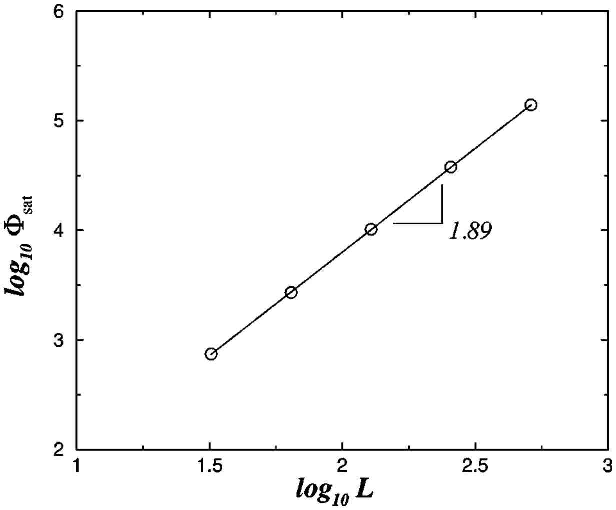

FIG. 2. Log-log plot of the saturation flux Φ_{sat} versus the system size L for critical percolation networks (circles). The straight line is the least-square fit to the data, with the number indicating slope $\alpha = 1.89 \pm 0.03$.

$$\Phi \sim L^{\alpha/2}\xi^{\beta}, \tag{10}$$

where β is a scaling exponent. From the least-squares fit to the $L=512$ data in the scaling region, we obtain $\beta = 0.34 \pm 0.02$. This value is consistent with the anomalous diffusion exponent, $1/d_w \approx 0.348$, observed for a random walk process in the two-dimensional sample-spanning cluster [4]. Such a correspondence can be explained by means of the following scaling argument [15]. If we consider that the penetration Λ in this regime should scale as $\Lambda \sim (Dt)^{1/d_R}$, where d_R is the critical exponent for diffusion reaction, and make use of re-

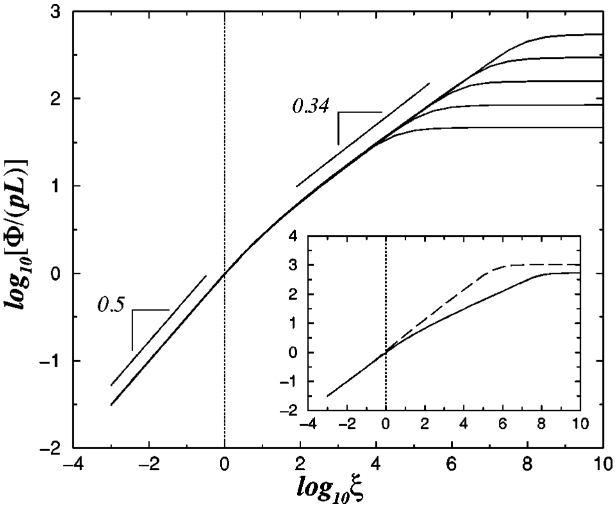

FIG. 3. Log-log plot of the rescaled flux $\Phi/(pL)$ versus the diffusion-reaction parameter ξ for critical percolation networks and $L=32$, 64, 128, 256, 512. The straight lines are the least-square fits to the data in the traditional and anomalous regions of diffusion reaction, with the numbers indicating slopes 0.5 and $\beta = 0.34 \pm 0.02$, respectively. For comparison, the inset shows the results for critical (solid line) and noncritical (dashed line) pore networks of size $L=512$.

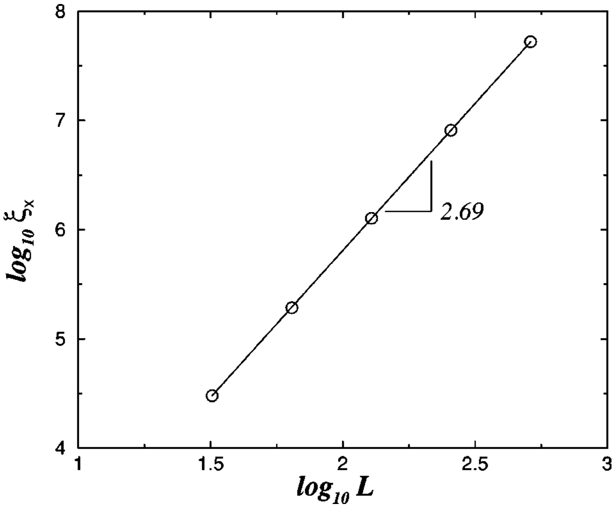

FIG. 4. Log-log plot of the crossover $\xi_\times$ versus the system size L for critical percolation networks (circles). The straight line is the least-square fit to the data, with the number indicating slope $z=2.69\pm0.03$.

lations $\Phi\sim L^{\alpha/2}\Lambda$ and $K\sim t^{-1}$, we obtain the time-independent relation $\Phi\sim L^{\alpha/2}\xi^{1/d_R}$. Accordingly, the critical exponent d_R should be equal to the two-dimensional random walk exponent on the incipient cluster, $d_w\approx2.87$. Indeed, this is consistent with the exponent obtained from our simulations, $d_R=1/\beta\approx2.94$. The inset of Fig. 3 reinforces the fact that the behavior of the system at criticality is markedly different from the diffusion-reaction response of the homogeneous network $(p=1)$ for $\xi>1$.

The value $\xi_\times$ at which the flux Φ crosses over from the power-law behavior Eq. (10) to the saturation regime of Eq. (9) provides another scaling signature for the diffusion-reaction process. Indeed, the logarithmic plot shown in Fig. 4 clearly indicates that $\xi_\times$ depends on the system size as

$$\xi_\times\sim L^z, \tag{11}$$

with an exponent $z=2.69\pm0.03$. At this point, we suggest that flux Φ follows the scaling relation [19]

$$\Phi\sim L^\alpha f\left(\frac{\xi}{L^z}\right), \tag{12}$$

where $f(u)$ is a scaling function [18]. As shown in Fig. 5, the data collapse obtained by rescaling Φ and ξ by L^α and L^z, respectively, confirms the validity of the scaling form (12). Furthermore, a direct relation among exponents α, β and z can be obtained. If we approach the crossover point from the left, we find $\Phi(\xi_\times)\sim L^{\alpha/2}\xi_\times^\beta$, while if we do it from the right, it follows that $\Phi(\xi_\times)\sim L^\alpha$. Comparing these relations, we obtain that $L^{\alpha/2}\xi_\times^\beta\sim L^\alpha$ and, from Eq. (11), it is possible to write the following scaling law:

$$\alpha=2\beta z. \tag{13}$$

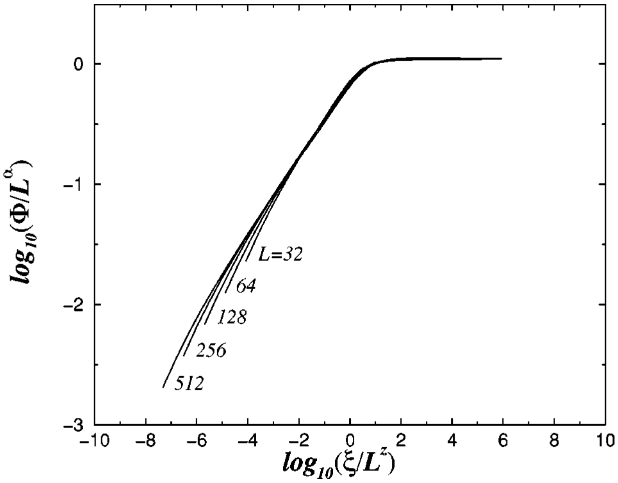

FIG. 5. Data collapse obtained by rescaling Φ and ξ with L^α and L^z, respectively.

Substituting into Eq. (13) the values found for β and z, gives $\alpha\approx1.83$, a value that is consistent with the calculated fractal dimension for the sample-spanning cluster, $\alpha=1.89\pm0.03$.

IV. CONCLUSIONS

The percolation theory certainly provides a useful model framework to study a large variety of systems displaying both structural disorder and statistical self-similarity. In particular, the percolation geometry has been frequently used as a conceptual paradigm for transport phenomena in poorly connected porous media. As mentioned in the Introduction, the present study has special relevance to the field of heterogeneous catalysis. For example, due to coke deposition, the gradual loss of connectivity in the active space of porous catalysts can impose severe drawbacks to the overall efficiency of the desired chemical reaction process. The situation can become even worse if the conversion of reagent at the pore level is limited by diffusive mechanisms of mass transfer. It is therefore important to elucidate the effect on the catalyst activity of the porous geometry in a marginal state of critical connectivity (e.g., at the percolation threshold).

In summary, we addressed the problem of diffusion and reaction processes occurring in two-dimensional pore networks at criticality. Our results show that, at an intermediate range of the parameter ξ, where the competition between diffusion and chemical reaction is relevant, the reactivity of the catalytic media is rather sensitive to the structural details of its pore space. Precisely, in this region, the reagent mass flux Φ penetrating the system displays scaling behavior $\Phi\sim L^{\alpha/2}\xi^\beta$, with an exponent $\beta\approx0.34$ that can be identified as the inverse of the random walk exponent for the sample-spanning cluster, $1/d_w$. Moreover, the finite-size scaling analysis of our simulation data, in the anomalous scaling and saturation regimes of diffusion reaction, reveals that it is possible to describe the behavior of Φ at moderate and large values of ξ in terms of scaling relation.

The implications of our results are manifold. An important one is related to the large discrepancy found between the diffusion-reaction behaviors of critical ($p=p_c$) and noncritical ($p=1$) pore networks, specially in the limited range of ξ values where the fractal geometry of the critical percolating structure has a marked influence on its diffusive characteristics. Our results give unambiguous evidence that the details of the pore space morphology can have a dramatic influence on the effectiveness of the porous catalyst. For instance, if the self-similar aspect of the material is not duly considered in the geometrical representation of the pore space, the consumption of reagent can be largely overestimated by any modeling approach to the diffusion-reaction phenomenon.

Another point of potential interest refers to the possibility of designing porous substrates for specific applications in heterogeneous catalysis. Clearly, we have presented here a typical case study in which the critical percolation geometry has a deleterious effect on the catalyst performance. However, other situations can arise where this type of morphology and a particular diffusion-reaction mechanism may combine to enhance the yield of a desired chemical species. This could be the case, for example, when *shape selectivity* effects associated with hindered diffusion mechanisms are capable of influencing a given reaction sequence taking place at the catalytic pore space [20–22]. Finally, we expect that this study can provide useful insight into the interpretation of the behavior of real catalysts.

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