Dynamic Scaling for the Fragmentation of Reactive Porous Media

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We introduce a simple model for the consumption and fragmentation of a reactive porous medium, and investigate various distinct regimes of such processes. The model simulates the reaction-consumption process in a realistic way, and is capable of simulating the entire range of possible kinetic limitations. We show that a dynamic scaling governs the time evolution of the fragment distribution, and calculate the critical exponents; these vary continuously with the reactivity of the porous medium. This dynamic scaling may also hold for the fragmentation of a system due to mechanical breakage, such as grinding of minerals, or stress-induced fragmentation of disordered solids, or of rocks and polymers.

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Fluid-solid reactions occur commonly in many natural and industrial processes involving porous media and have important scientific and technological implications.[1] Examples include catalyst deactivation,[2,3] noncatalytic gas-solid reactions,[4] enzyme immobilization,[5] and hindered (restricted) diffusion and reaction in porous catalysts.[6,7] In many instances the chemical reaction consumes the solid matrix of the porous medium leading eventually to total consumption and disappearance of the solid matrix, as in the case of char or coal gasification and acid rock dissolution.[8] In other instances one or more reaction products are deposited on the solid matrix resulting in decreased intrinsic reactivity and blockage of the porous structure. This is the case with catalyst deactivation.[2,3] It is the first problem that is of interest here.

In this Letter we analyze the consumption of a porous solid by a chemical reaction between the solid matrix and a reactant and the resulting changes in the structure of the solid. The porous solid is represented by a percolation cluster (i.e., each site of the lattice belongs to the solid matrix with probability p). To study this phenomenon one has to realize that there are two distinct regimes of the reaction-consumption process. If the consumption rate is limited only by the chemical reaction rate, then one is in the kinetic regime (KR). In this regime, the concentration of the reactants outside the porous solid is the same everywhere and the external solid surface of the porous medium is totally exposed to the reactants. On the other hand, if the consumption rate is limited by the rate of diffusion of the reactants, only the most exposed part of the solid matrix is reached and consumed by the reactants. As a result even if one starts with a porous medium with a very irregular surface, the diffusion-reaction-consumption process makes the external surface of the system smooth. Therefore, after some time the irregular system develops a very smooth external surface, which ultimately takes a spherical shape and its radius shrinks uniformly.

An important consequence of the process just described, both in the KR and the diffusion-limited regime (DLR) when the reactivity is low, is the phenomenon of fragmentation. If the consumption of the solid matrix is continued for a long enough time, it will disintegrate into finite clusters (fragments), which have a wide variety of shapes and masses. If the reaction-consumption process continues even after the initial fragmentation has taken place, the number and mass of the fragments will eventually decrease with time. This decrease in the number of clusters is somewhat similar to cluster-cluster aggregation (CCA) processes,[9] for which a dynamic scaling for the number of clusters of a given size has been developed.[10] There are, however, significant differences between the phenomenon studied here and that of CCA. Whereas the system in the latter process is conserved (i.e., total number of occupied sites does not change), and a large fractal structure is eventually formed, the former phenomenon is "dissipative" in the sense that the density of occupied sites *decreases with time* and eventually vanishes, so that it can be considered as a *disaggregation* process. As may be obvious, such disaggregation and fragmentation processes are also different from polymer-chain degradation processes,[11] where a completely different mechanism is responsible for the degradation of the polymer chain. Despite these differences, we show that a dynamic scaling holds for the distribution of fragments.

As the process time increases the number of fragments also increases, reaches a maximum, and then ultimately vanishes as the fragments are consumed. Of course each individual cluster does not have to be in an environment where a specific regime is dominant, because the reactants may reach some of the fragments faster and easier than others. However, we neglect such complications here. To describe the evolution of fragment size distribution and the decrease in the number of clusters we hypothesize that

$$n_s \sim t^{-w} s^{-\tau} f(s/t^z), \tag{1}$$

where n_s is the number of fragments (per lattice site) of s sites and w, z, and τ are (presumably) universal critical exponents. Here $f(x)$ is the scaling (or cutoff) function whose shape is presumably universal. Equation (1) has the same form as that proposed for the CCA processes.[10] However, in the CCA the total number of clusters $N(t)$ *decreases monotonically,* whereas in the present model $N(t)$ *has a maximum.* Since the density ρ of the occupied sites (e.g., the solid sites in the present model) is given by

$$\rho \sim t^{-w} \int_0^\infty s^{-\tau+1} f(s/t^z) ds \sim t^{-w+(2-\tau)z}, \tag{2}$$

it follows that for the CCA one has $w=(2-\tau)z$, since ρ remains constant. In the present problem $\rho \to 0$ as $t \to \infty$, which only means that

$$w > (2-\tau)z. \tag{3}$$

Moreover, the mean cluster size $S(t)$, which is given by $S(t) \sim t^z$ *vanishes* in the present problem and thus $z<0$, in contrast with the CCA processes where $S(t) \to \infty$ as $t \to \infty$ and thus $z>0$.

We have investigated this phenomenon in both the KR and the DLR within a unified model, and have estimated the exponents w, z, and τ using the following model. We start with a L^d network (d is the dimensionality) and generate the largest percolation cluster,[12] which represents the solid matrix, and introduce reactive molecules (e.g., oxygen) on the external surface of the lattice, far from the solid matrix. These molecules perform an unbiased random walk on the empty sites of the lattice, and interact with each other with hard-core interactions and, thus, double occupancy of the sites of the lattice is not allowed. If a molecule hits a solid site it reacts with it with probability r, which essentially represents the reactivity of the solid matrix. If reaction does take place, the reactant molecule disappears and a fraction of the solid site is consumed. Since in our model we use finite lattices in order to represent real systems (e.g., char particles of micron size), each site should represent a macroscopic mass unit. Thus each site has to be hit by the molecule, in a reactive collision, M times (where M is a model parameter) before it is totally consumed. The results presented below are for $M=1$; the results for $M>1$ and for cases where each site has different reactivity (i.e., the probability of reaction changes from site to site) will be reported elsewhere.[13]

The overall behavior of the system strongly depends on the reaction probability r. If $r \simeq 1$, then only the most exposed part of the solid matrix ("hottest sites" in the language of growth processes[14]) are consumed at the initial stages of the process. The net effect is the removal of all irregularities of the external surface of the solid matrix, making its shape smooth and regular. This is indeed what we find in our simulations, which is also in agreement with simulations with other model systems.[15] As a result, no major breakup of the solid matrix takes place and no fragments of appreciable size are formed. On the other hand, if r is small the reactant molecules are able to penetrate deep into the pore space and hit and consume the weak points of the solid matrix, which are links in the percolation cluster[16] that connect the large blobs of multiply connected sites. As a result, for small r solid-matrix fragmentation takes place and many clusters with a wide variety of shapes and sizes appear and the dynamic scaling discussed above develops. It is obvious that the limits $r=1$ and $r \simeq 0$ represent, respectively, the DLR and the KR. In particular for very low values of r and because of the deep reactant penetration into the pore space, the concentration of the reactant in the vicinity of the solid matrix becomes everywhere uniform, i.e., one is in the kinetic regime.

The most interesting part of the process is when one starts with the largest percolation cluster at the percolation threshold p_c (where[17] $p_c \simeq 0.59275$ for the square lattice and $p_c \simeq 0.3116$ for the simple-cubic lattice). At this point the cluster has a fractal structure at all length scales and, therefore, the phenomenon studied here can be considered as an example of breakup and fragmentation of fractal surfaces. Simulations with $p > p_c$ have also been performed, and the long-time results are similar to those discussed for $p = p_c$. The exponent that is of prime interest here is w, because it has recently been possible[18] to measure w experimentally for char gasification processes. Most of our simulations were done on a square lattice with $L=300$ and a simple cubic lattice with $L=50$, and we typically averaged the results over 10 different realizations of the lattice.

In Fig. 1 we present the variation with time of the total number of clusters $N(t)$ for different values of r (the results are for the square lattice). Here each cluster has more than one site. At the beginning of the process $N(t)$ increases, reaches a maximum, and then decreases and ultimately vanishes. Around the maximum of $N(t)$ some small oscillations were observed. This is due to the

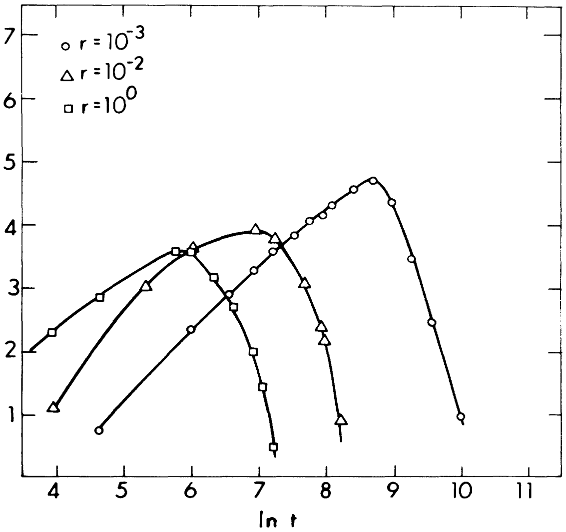

FIG. 1. The dependence of the total number of fragments $N(t)$ on the time t for selected values of the reactivity r. Solid lines are guides to the eye.

fact that when a relatively large cluster is hit by several reactant molecules it can fragment into several smaller clusters and, therefore, $N(t)$ can temporarily increase. Eventually of course, all relatively large clusters disappear and $N(t)$ decreases monotonically. For $r=10^{-3}$, a great number of clusters, some very large, are formed. For very small values of r (e.g., $r \simeq 10^{-5}$) the system reaches a steady state, which means that $r \simeq 0$ does indeed represent the KR. In the limit of $r=1$, no major breakup of the original large cluster takes place, and all of the clusters are very small (no more than a few sites).

In Fig. 2 we present the cluster size distribution at a fixed s for various values of r. Again there is a qualitative difference in n_s as r varies. One finds that the exponent w depends on r. For example, $w \simeq 10$ for $r=0.01$, whereas $w \simeq 0.3$ for $r=1$. We also determined the cluster distribution n_s for fixed values of t and determined the exponent τ, and verified that the inequality (3) is satisfied (details will be given elsewhere[13]). As was the case for w, the exponent τ also appeared to depend on r. It should be pointed out that if we plot the cluster size distribution at a fixed but large value of s (e.g., $s \simeq 15$), the curve corresponding to $r=1$ will completely disappear, because in the DLR no large cluster is formed. These features are all in agreement with experimental observations.[18,19] This is the first time that a unified model can accomplish this.

One of the outstanding problems in interpreting the existing experimental data in gas-solid reactions has been the nature of the regime in which the reaction, and the consequent consumption of the solid, takes place. Our model and simulations can provide a definitive answer to this problem. As discussed above, by varying the reaction probability r one can span the entire spectrum of the reaction-consumption regimes, from the KR (for $r \simeq 0$) to the DLR (for $r \simeq 1$). For example, we performed our simulations on a simple-cubic lattice, with the initial fraction of the solid sites $p \simeq 0.65$ and the reaction probability $r \simeq 10^{-2}$. We then obtained $w \simeq 1$, which is in agreement with the recent experimental data[18] (details of the comparison will be given elsewhere[13]). This agreement may indicate that the experimental system was close to the KR, but diffusional limitations were also important to some extent. At this point, however, this agreement is tentative since a more sensitive study on the effect of the initial conditions (initial cluster) should be performed. In particular, one has to establish clearly that the morphology of a char particle can be described by a percolation cluster. We believe, however, that the dynamic scaling proposed here can, in principal, determine the nature of the regime of reaction-consumption process. Moreover, the model developed here predicts, for small values of r, the existence of a maximum in the reaction rate (fraction of solid sites consumed per unit of time) at some well-defined value of conversion (fraction of sites consumed up to time t), in agreement with experimental observations.[18,19] Thus, all important features of such processes are reproduced here.

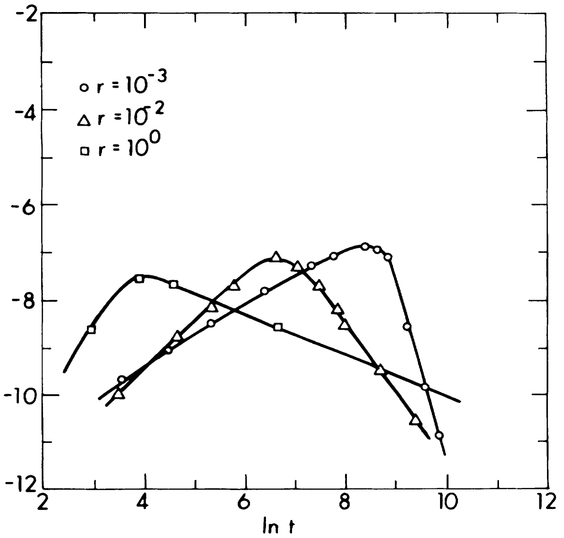

FIG. 2. The cluster size distribution $n_s(t)$ vs t for $s=4$. If n_s is plotted for higher values of s, the corresponding curve for $r=1$ will completely disappear, because in the DLR no large cluster is formed.

We note that a simple model of fragmentation of reactive porous media, in the KR, has recently been developed[20-23] in which one identifies the solid sites which are adjacent to the external (open) perimeter sites. These sites are all consumed in one unit of time and redesignated as open space (pores). The new solid sites that are adjacent to the perimeter sites are now identified and consumed and so on. Thus one has a simple model of disaggregation[24] for random surfaces. Although a dynamic scaling also holds for fragmentation during this process,[20,21] the results do not agree quantitatively with the experimental data, and adjustable parameters must be introduced in order to make the agreement quantitative.

Finally, we note that it has recently been suggested that the surface of fractal structures requires an infinite hierarchy of fractal dimensions for its complete characterization.[14,25] To measure these fractal dimensions one uses particles following random-walk trajectories. Each particle is started off at a random position outside the area occupied by the fractal system and its trajectory is followed until it reaches a perimeter site (a process similar to what is described here). A measure of the surface size can then be obtained based on the distribution of the total number of times each perimeter site has been hit after a large number of diffusing particles have been released. Since in the present problem the reaction rate is proportional to the total number of surface sites that have been hit by the diffusing particles, we expect that in the DLR the scaling of the reaction rate is directly related to the moments of the distribution of the number of times that perimeters sites have been visited.[13] On the other hand, we do not see any direct connection between the exponents w and τ and these fractal dimensions, as w and τ are dynamic exponents, whereas such fractal dimensions are static quantities.

In summary, we have introduced here a model for the fragmentation of chemically reactive surfaces. The model reproduces all of the important features of such phenomena that have been observed experimentally. We have shown that a dynamic scaling governs the evolution of the fragment size distribution. Although this dynamic scaling was developed for reactive surfaces, it also holds for any process in which a fragmentation of the solid matrix takes place as a result of mechanical breakage,[13] such as grinding of minerals or stressed-induced fragmentation of rocks[26] or of polymers and disordered solids[27]; our preliminary results[13] support this assertion. A detailed study of these phenomena will be reported elsewhere.[13]

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