Phase transitions and crossovers in reaction-diffusion models with catalyst deactivation

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The activity of catalytic materials is reduced during operation by several mechanisms, one of them being poisoning of catalytic sites by chemisorbed impurities or products. Here we study the effects of poisoning in two reaction-diffusion models in one-dimensional lattices with randomly distributed catalytic sites. Unimolecular and bimolecular single-species reactions are considered, without reagent input during the operation. The models show transitions between a phase with continuous decay of reactant concentration and a phase with asymptotic non-zero reactant concentration and complete poisoning of the catalyst. The transition boundary depends on the initial reactant and catalyst concentrations and on the poisoning probability. The critical system behaves as in the two-species annihilation reaction, with reactant concentration decaying as $t^{-1/4}$ and the catalytic sites playing the role of the second species. In the unimolecular reaction, a significant crossover to the asymptotic scaling is observed even when one of those parameters is 10% far from criticality. Consequently, an effective power-law decay of concentration may persist up to long times and lead to an apparent change in the reaction kinetics. In the bimolecular single-species reaction, the critical scaling is followed by a two-dimensional rapid decay, thus two crossovers are found.

I. INTRODUCTION

Simple models for reactions of diffusing species have been intensively studied in the last decades [1, 2, 3], such as trapping reactions, annihilation or coagulation of a single species and two-species annihilation. In low dimensions, these apparently simple models yield a wide range of nontrivial kinetic behaviors because mean-field theories (laws of mass action) fail. One-dimensional media may be a realistic description of the structure of catalysts with long and narrow pores, such as zeolites and porous oxides, or may represent step edges of two-dimensional surfaces where reactants preferentially adsorb. The former materials have inhomogeneous distributions of catalytic centers where the reactions take place, which motivated recent theoretical models. If the reaction is unimolecular with volatile products, then the inhomogeneity can be represented by trapping models [4, 5, 6], with the traps playing the role of catalytic sites. For other reaction mechanisms, the disorder in the spatial distribution of the catalytic centers was also considered in recent works [7, 8, 9, 10, 11]. In some cases, it leads to nontrivial dependence of the reaction rates on diffusion coefficients and catalyst density. Effects of catalyst geometry and conditions to improve the efficiency of a reaction process were also discussed in recent works [12, 13, 14].

A phenomenon of great economic impact on industrial processes is catalyst deactivation, which is the reduction of catalytic activity due to blocking of active sites, distortion or blockage of the porous structure, sintering of metal particles etc [15, 16, 17]. One of the possible deactivation mechanisms is poisoning. It occurs when a reactant, product or impurity is strongly chemisorbed in the active sites, preventing further reactions but not affecting the diffusion of reactants and products along the pores. For instance, poisoning of metals by sulphur species ($H_2S$, $SO_2$, $SO_4^{2-}$ etc) is a problem in many catalytic processes, such as hydrogenation, methanation, Fischer-Tropsch synthesis, steam reforming and fuel cell power production. In other cases, large aggregates are formed inside the catalyst pores; this is called coking or fouling and eventually leads to pore blockage. Due to its technological relevance, deactivation mechanisms are frequently included in models of catalytic processes [15, 18]. The main interest of those models is to predict the time evolution of the catalytic activity and the turnover frequency with a continuous flux of reactants, thus they are usually designed for a particular application.

However, there is no systematic study of the effects of deactivation on the kinetics of simple reaction-diffusion models (e.g. trapping or annihilation). The aim of this work is to fill this gap by introducing one-dimensional models for catalyzed reactions of diffusing reactants with poisoning of catalytic sites. We will consider initial conditions with uniform distributions of reactants and no external flux. These conditions are far from those encountered in real catalytic processes in porous media, but they are interesting as a first step to understand possible changes in those systems kinetics.

We will study these models with scaling concepts supported by numerical simulations. Unimolecular and bimolecular (same species) reactions occurring upon contact of the reactants with the catalytic sites are considered. Poisoning is represented by the permanent blockage of those sites, with a given probability, immediately after the reaction takes place. Two limiting cases of this type
of model anticipate the presence of kinetic transitions: for very low deactivation rates and low initial reactant concentration, poisoning is negligible, thus that concentration decays similarly to the case without deactivation; however, for high deactivation rates and high initial reactant concentration, the catalyst will be rapidly poisoned and part of the reactants will not be consumed. This analysis raises the question of how these systems behave when deactivation rates, initial reactant concentrations and catalyst loadings change, and which types of transition occur.

We will show that two phases exist in those systems. In one phase, the reactant concentration continuously decay to zero, with the same asymptotic scaling of the main reaction. In the other phase, there is a non-zero reactant concentration at long times. In the boundary between those phases, the system behaves as in the two-species annihilation reaction, with reactant concentration decaying as $t^{-1/4}$ in one dimension - the catalytic sites play the role of the second species in this case. Near a transition point, we will show a long crossover to the asymptotic scaling of the phase of decaying reactant concentration. Thus, a correct interpretation of the main reaction kinetics becomes difficult, particularly with short time simulation data. For bimolecular reactions, the deactivation also enlarges the time interval of an intermediate two-dimensional scaling, where the concentration decay is faster than both the short-time and the long-time ones. These crossovers may also have important consequences in the interpretation of experimental results.

The rest of this paper is organized as follows. In Sec. II we consider unimolecular reactions with inert products taking place at random catalytic sites (traps) subject to deactivation. In Sec. III, bimolecular single-species reactions are considered and in Sec. IV we summarize our results and present our conclusions.

II. TRAPPING REACTIONS WITH TRAP DEACTIVATION

In this model, defined in a one-dimensional lattice, we consider unimolecular reactions with volatile products, which occur when the reactant is in contact with the catalyst. Initially, catalytic sites (C) are randomly distributed with coverage $\sigma_0$ and are immobile. The other sites are labeled as non-catalytic or empty sites. At $t = 0$, a concentration $\theta_0$ of reactants (species A) is randomly distributed through the non-catalytic sites - consequently, the condition $\sigma_0 + \theta_0 \leq 1$ is obeyed. For $t > 0$, reactants A diffuse with coefficient $D$, i. e. each reactant executes an average of $D$ random steps to neighboring sites per unit time (the lattice parameter is the length unit), and they obey the excluded volume condition.

The unimolecular reaction corresponds to a trapping reaction \[ A + C \to C, \] in the form which immediately occurs when A occupies the same site of C. With probability $p$, the catalytic site is deactivated, i. e. C is converted into an empty site (consequently, it does not affect diffusion of the other reactants). The reaction with subsequent poisoning corresponds to the reaction scheme

\[ A + C \to 0, \]

where 0 represents an empty site. Thus, the model may be viewed as a competition between the reaction (1), with probability $1 - p$, and the reaction (2), with probability $p$. This is illustrated in Fig. 1a.

As time evolves, the catalyst coverage and the reactant concentration are respectively denoted by $\sigma (t)$ and $\theta (t)$.

We performed simulations of this model in lattices of length $N = 2^{20}$ (more than one million sites), with several different values of the parameters $\sigma_0$, $\theta_0$ and $p$. For each set of parameters, typically $10^6$ different realizations were averaged. Diffusion coefficients of species A were $D = 1$ in most cases. Maximum simulation times were up to $10^8$ units under these conditions.

A. Long time scaling

For $p = 0$, we recover the well-known trapping problem with static traps. Since there is no deactivation, all the reactants initially placed in a segment between two consecutive traps are annihilated in one of the edge traps. For a fixed segment size $L$, the decay is a simple exponential in $t^{1/2}/L$. However, the average over (Poisson
(3)

where $\rho$ is the trap density and $a = 3/2(2\pi^2)^{1/3}$. In the case $p = 0$, we have $\rho = \sigma_0$.

For $p$ small but non-zero, the concentration of reactants rapidly decays to very low values, while only a fraction of the initial catalytic sites is deactivated. The annihilation of a concentration $\theta_0$ of species A leads to poisoning of a density $p\theta_0$ of catalytic sites. Thus, at long times, the trap density is $\sigma = \sigma_0 - p\theta_0$ and the reactant concentration $\theta$ is much smaller. In this case, reaction (3) is asymptotically dominant, thus a decay as in Eq. (3) is expected.

Simulations with small values of $p$ confirm this result, as shown in Fig. 2a. They also show another interesting and somehow surprising feature: while results for $p = 0$ show significant corrections to the dominant scaling (Eq. 3), the results for non-zero $p$ show that stretched exponential decay with negligible corrections (the data for $p = 0.1$ in Fig. 2a fits a straight line in three time decades). The corrections for $p = 0$ were observed in previous simulation work [1], and for this reason it took many years for the original analytical prediction in two and three dimensions [4] to be confirmed numerically [6].

From the above discussion, we expect the same asymptotic behavior for any initial condition where $\sigma_0 > p\theta_0$. On the other hand, if $\sigma_0 < p\theta_0$, a finite reactant concentration $\theta = \theta_0 - \sigma_0/p$ is found at long times, while the trap density continuously decays. This regime is dominated by reaction (2), with excess concentration of A relative to C. Fig. 2b confirms this result for $\theta_0 = 0.4$, $\sigma_0 = 0.15$ and $p = 0.7$, which gives a remaining density of reactants $\theta \approx p\theta_0$.

A transition is found when

$$\sigma_0 = p\theta_0,$$

which corresponds to a surface in the $(\sigma_0, \theta_0, p)$ space. In this case, the reactant concentration and the catalyst coverage decrease by the same factors at all times.

The continuous increase of the distance between consecutive catalytic sites certainly rules out the arguments that lead to the result in Eq. (3). Instead, in a transition point this system resembles the two species annihilation reaction of Eq. (2) with balanced concentrations of species A and C. According to previous work [1,19], in the reaction (2) with equal initial concentrations $\rho_0$ of A and C in one dimension, the reactant concentration $\rho$ decays as

$$\rho \sim \frac{\rho_0^{1/2}}{([D_A + D_C]t)^{1/4}},$$

where $D_A$ and $D_C$ are diffusion coefficients. Note that this scaling law does not change if one species is static, which is the case of the catalyst C in our model.

The decay as $t^{-1/4}$ is confirmed for several transition points, as shown in Fig. 3. However, the dependence with the initial reactant concentration is different from the square-root law of Eq. (5): for fixed $\sigma_0$, $\theta$ is proportional to $\theta_0$. This occurs because the kinetics leading to Eq. (5) is a balanced annihilation of AC pairs, but in our model the annihilation of an AC pair requires trapping of $1/p$ reactants (A) in the average. Thus, $\rho_0$ must be replaced by $\theta_0/p = \theta_0^2/\sigma_0$ in Eq. (5).

B. Crossover scaling

Here we focus on the case where the system is near the critical surface (Eq. 4) but $p < p_c = \sigma_0/\theta_0$, i.e. there is a continuous decay of the reactant concentration. At short times, this decay follows the critical power law of Eq. (5), but it crosses over to the stretched exponential behavior (Eq. 3) at long times. This is illustrated in Figs. 4a and 4b for fixed values of $\sigma_0$ and $\theta_0$ and various $p$.

One interesting point is that, even with one parameter being 10% distant from the critical value (e.g. $p = 0.34$ in Fig. 4a), the concentration decay for $\theta > 10^{-4}$ still resembles a power law. The exponent of this ap-
At long times, the remaining density of catalytic sites is proportional to \( p_c - p \). Eq. (3) gives a reactant concentration

\[
\theta \sim \exp \left[ -b(Dt)^{1/3} \right], \quad b \sim (p_c - p)^{2/3}.
\] (6)

However, the scaling of \( \theta \) on \( p_c - p \) is difficult to be confirmed numerically (e.g., in Fig. 4b) because the data close to \( p_c \) shows huge corrections to the (noncritical) asymptotic decay of Eq. (3).

From the above result, we can estimate the time in which the apparent power law decay crosses over to the exponential one. Matching the time scaling in Eqs. (3) and (5) (the latter with no amplitude depending on \( p_c - p \)), we obtain a crossover time of order

\[
t_c \sim (p_c - p)^{-2/3} \ln (p_c - p)^{1/3}.
\] (7)

This helps to understand the long crossover in this system: for the values of \( p \) shown in Figs. 4a and 4b, we expect \( t_c \) to range approximately from \( 10^4 \) to \( 10^7 \). Experimentally, it has an important consequence: the reaction kinetics may be incorrectly identified if one observes the time evolution of the concentration decay (or the turnover rate) in a restricted time range and disregards the effects of deactivation.

### III. ANNihilation REACTIONS WITH Trap DEactivation

The second reaction mechanism studied in this work is bimolecular with a single species. The model corresponds to annihilation reactions of this species limited to catalytic sites of a lattice.

Again we consider initial random distributions of static catalytic sites \( C \), with coverage \( \sigma_0 \), and diffusing reactants \( A \) with initial concentration \( \theta_0 \). The bimolecular reactions between two \( A \) which meet at a catalytic site is represented by

\[
A + A + C \rightarrow C, \tag{8}
\]

It corresponds to the well known one-species annihilation model \( (A + A \rightarrow 0) \) restricted to the set of catalytic sites, as in Ref. [3]. The poisoning is also represented by the permanent blockage of a catalytic site after a reaction, and occurs with probability \( q \). It corresponds to the reaction

\[
A + A + C \rightarrow 0. \tag{9}
\]

The competitive model is illustrated in Fig. 1b.
A. Long time scaling

When \( q = 0 \), we have the model proposed by Oshanin and Blumen \[2\], in which the density of reactants decays as

\[
\theta \sim 1/(D\theta)^{-1/2}
\]

in one dimension. This dominant contribution to the decay does not involve the catalyst coverage, which can be explained as follows. The characteristic time for two consecutive reactants to meet at the same site is

\[
\tau_{AA} \sim 1/(D\theta^2).
\]

After they meet, the closest trap is inside a neighborhood of size \( 1/\sigma \). Thus, the typical time for those reactants to meet at that trap is \( \tau_{AAC} \sim 1/(D\sigma_0^2) \). At long times, \( \theta \ll \sigma_0 \), thus we have \( \tau_{AAC} \ll \tau_{AA} \) and the long-time scaling is dominated by \( \tau_{AA} \), which leads to Eq. \( \theta \). However, the catalyst coverage plays an important role at intermediate times, as will be shown in Sec. III B.

For small \( q \), we expect the same scaling as in Eq. \( \theta \). At long times, \( \theta \ll \theta_0 \), thus the density of annihilated A particles tends to \( \theta_0 \) and a density \( q\theta_0/2 \) of catalytic sites will be deactivated. Thus, the final catalytic coverage is \( \sigma_0 - q\theta_0/2 \). Simulation results shown in Fig. 5 confirm these predictions.

![Decay of reactant concentration far from the critical boundary for the bimolecular single-species model with \( q = 0.1 \) and \( q = 0.1 \) (circles). The dashed line shows a decay as \( t^{-1/2} \).](image)

We expect a transition between a phase of decaying reactant concentration and a phase of non-zero long time concentration when

\[
\sigma_0 = q\theta_0/2.
\]

In this critical surface, reactant concentration and catalyst coverage decrease by the same factors as time increases.

The three-particle reaction \[3\] and an analogy with the case of Sec. II could suggest that the scaling of the concentration at the transition point is that of a three-particle annihilation model. Since the catalyst coverage does not play a role in the decay for \( q = 0 \) (Eq. \( \theta \)), we might think that the time \( \tau_{AA} \) governs the scaling at the transition. However, this is not the truth. Similarly to the unimolecular case of Sec. II, there is accumulation of C at some regions where the initial concentration of A was locally small. Also, there is accumulation of A at neighboring regions, where its initial concentration was locally high. Thus, the coarsening is again dominated by the annihilation time of neighboring domains, which scale as \( 1/\theta^2 \) \[1, 19\], and not by the time \( \tau_{AA} \). Thus, this transition also scales as in two-species annihilation model, although three particles are involved in the reactions \[8\] and \[9\].

These conclusions are supported by simulation results. In Fig. 6a, we show the average number of consecutive A, \( \langle S_A \rangle \), and of consecutive C, \( \langle S_C \rangle \), as function of time, in one point of the critical surface. They scale approximately as

\[
\langle S_A \rangle \sim \langle S_C \rangle \sim t^{1/4}.
\]

![Decay of the reactant concentration approximately as \( t^{-1/4} \) (Eq. \( \theta \)).](image)

In Fig. 6b, we observe that the critical \( \theta \) depends on the initial concentration in the same way as the unimolecular reaction, i. e., with \( \rho \) in Eq. \( \theta \) replaced by \( \theta_0/q \sim \theta_0^2/\sigma_0 \).

For \( \sigma_0/2 < \theta_0 \), the catalyst coverage vanishes asymptotically, while a finite number of reactants is present. The final (non-consumed) reactant concentration is \( \theta_0 - 2\sigma_0/q \). These results were also confirmed by simulation.

B. Crossover scaling

The above analysis suggests that a crossover between two power law decays \( t^{-1/4} \) and \( t^{-1/2} \) would be observed near a transition point. However, again the situation is much more complex. Ref. \[7\] analyzed the problem with \( q = 0 \) (no deactivation) and showed that, for small catalyst concentration, there is a long time interval with effective two-dimensional decay of the concentration:

\[
\theta \sim \ln t/t.
\]

Small catalyst concentration is actually the case as we approach the critical point. Consequently, not only two but three scaling regions are expected: for short times, the critical decay as \( t^{-1/4} \), while the orders of magnitude of \( \sigma \) and \( q\theta/2 \) are not very different (see Eq. \( \theta \)).
intermediate times, the much faster power law decay of Eq. 13 for $t \gg 1/\sigma_{\infty}^2$, where $\sigma_{\infty}$ is the asymptotic concentration of the catalyst, the asymptotic scaling is found. Since $1/\sigma_{\infty}^2 \sim (q_c - q)^{-2}$ near criticality, the deactivation significantly enlarges the time window of the intermediate scaling.

These results are illustrated in Fig. 7 for several values of $q$. For $q = 0.21$, (16% far from criticality), a very long intermediate regime is observed, and the asymptotic decay of Eq. 14 is found only for $t \gg 10^6$ and concentrations below $10^{-4}$. Note that this decay is not dependent on initial concentrations, as shown by the data for $q = 0.21$ and $q = 0.22$. Closer to the critical point, the asymptotic decay is not observed even with concentrations below $10^{-4}$. Compared to the unimolecular reactions (Sec. II), finding the true reaction kinetics from reactant or product concentration data is much trickier in this case due to the presence of two crossovers.

IV. DISCUSSION AND CONCLUSION

We studied reaction-diffusion models in heterogeneous one-dimensional lattices with catalytic and non-catalytic sites and possible deactivation of catalytic sites by poisoning. These models show a transition between a phase with continuous decay of reactant concentration and survival of catalytic sites, and a phase with asymptotic non-zero reactant concentration and complete poisoning of the catalyst. The critical systems behave as the two-species annihilation model with stoichiometric concentrations of reactants. For each reaction mechanism, the transition boundary depends on the initial concentrations of reactant and catalyst and the probability of deactivation. We analyzed models of unimolecular and bimolecular single-species reactions, and showed that, in a transition point, the reactant concentration decays as in the two-species annihilation reaction. In the decaying phase but near a critical point of the unimolecular reaction, a
long crossover to the asymptotic scaling is found. Thus, short time simulations show effective power-law decays instead of the stretched exponential, which suggests a change in the reaction kinetics. The situation is much more complex with the bimolecular single-species reaction because the small catalyst density near a critical point leads to an apparent two-dimensional decay of reactant concentration. Thus, two crossovers are observed and the asymptotic decay is found only at extremely long times, even with one parameter being more than 10% far from criticality.

Our results resemble transitions in other competitive reaction-diffusion models which were not explicitly interpreted as effects of catalyst deactivation. Sanchez and coworkers studied the case where reaction \( A + B \rightarrow B \) competes with \( B + C \rightarrow C \) (double trapping) or \( B + C \rightarrow 0 \) (trapping plus annihilation) \[28, 29\], showing that the initial concentrations and the reaction rates also determine the asymptotic behavior. Further work on these and related reactions also considered anisotropic or anomalous diffusion of reactants, different forms of reactant input, and power-law decays of reaction rates, which lead to a wide range of interesting kinetic behaviors \[30, 31, 32, 33, 34, 35\]. For instance, the model of Yuste et al. \[33\] for trapping by subdiffusive traps with vanishing density shows a transition with scaling similar to our unimolecular model.

Despite the simplicity of the reaction-diffusion models presented here, experimental applications are possible. For instance, the depletion zones of a trapping model with a single trap were already observed in photobleaching of fluorescein dye by a focused laser beam \[34, 35\], and models with competitive reactions were already used to represent patterns of a reaction between \( \text{Cr}^{3+} \) and Xylenol Orange \[36\]. Thus, we believe that our work may also have applications to systems with catalyzed reactions and deactivation by poisoning, particularly to help the interpretation of kinetic data.

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