

Reactive dynamics on two-dimensional supports: Monte Carlo simulations and mean-field theory

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Monte Carlo simulations and mean-field models are used for the study of nonequilibrium reactions taking place on the surface of a catalyst. The model represents the catalytic reduction of NO with H₂ on a Pt surface. Both Monte Carlo simulations and mean-field results predict the existence of a critical surface in the parameter space where the catalyst remains active for long times. Outside this critical region the catalyst remains active for finite times only. A discrete version of the mean-field model is proposed that takes into account the discrete, two-dimensional nature of the catalyst. For homogeneous initial conditions this improved model provides better quantitative agreement with the Monte Carlo results.

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I. INTRODUCTION

To describe the complex dynamical behavior of reactive processes taking place on catalytic supports, it is necessary to take into account detailed interactions between neighboring species, local fluctuations, and the geometric properties of the support [1–9].

The widely used mean-field models [10] are successful in describing homogeneous, well mixed systems and cannot adequately describe processes governed by local effects and fluctuations. In particular, for catalytic processes where the reactivity takes place on the two-dimensional surface of the catalyst and where diffusive mixing is restricted, mean-field models normally fail to reproduce the experimental results. Instead, numerical Monte Carlo and lattice-gas models can be designed that take into account local properties of the lattice and the finite range of the interactions [1–9]. Due to their detailed character, these models are successful in reproducing the rich variety of mesoscale pattern formation as well as the complex dynamics of catalytic processes [8,9].

A very successful Monte Carlo model that describes the catalytic oxidation of carbon, $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ on the Pt catalytic surface, was introduced by Ziff, Gulari, and Barshad in 1986 [3]. This minimal model predicts that the system undergoes kinetic phase transitions [3–8], which correspond to poisoning phenomena seen in catalytic experiments [11–13].

A different catalytic reaction that presents complex kinetics is the NO reduction with H₂ that also takes place on the surface of Pt catalyst. In this reaction multiple steady states, poisoning, and kinetic oscillations are observed [14]. The activity of the reactions depends on the partial pressure of the reactants $P_{\text{H}_2}/P_{\text{NO}}$, on the surface temperature and on the surface reconstruction. Poisoned states are observed for low temperatures (e.g., for temperatures below 250 K the adsorp-

tion of H₂ leads to hydrogen-covered catalyst), while for high temperatures the surface is covered by NO (NO dissociation becomes negligible) [14]. Phase transitions of the catalyst between the square and the hexagonal lattice configurations and kinetic oscillations were found between 430 and 445 K [13,14].

In the current study a simple chemical scheme is examined, which is inspired from the NO reduction on the surface of Pt catalyst [15–18]. The scheme uses only bimolecular reactive steps and there are no autocatalytic processes. In addition the model is *lattice compatible*. This means that the number of particles on the catalytic surface together with the empty catalytic sites are conserved throughout the process. This condition is necessary in order to have a meaningful lattice model. Because of its minimal character this model does not address the problems of oscillatory kinetics and of lattice phase transitions observed in a range of temperatures in the NO reduction on Pt surface [15–19]. However, it predicts different equilibrium regimes separated by a critical surface on the parameter space. Furthermore, this simple model predicts that near criticality the catalyst remains active for long times, whereas away from criticality a “frozen” state is soon reached where the catalytic surface is “poisoned” by reactants or products.

In Sec. II the minimal lattice compatible chemical scheme is introduced. In Sec. III Monte Carlo simulations are shown and the phase space is explored to determine different equilibrium regimes. In Sec. IV the mean-field kinetic equations are presented and the phase space properties are discussed. Qualitative agreement is reached between the mean-field results and the Monte Carlo simulations. In Sec. V an improved mean-field approach is proposed by truncating the Master equation, which takes into account only interactions with nearest neighbors. This improved approach better predicts the Monte Carlo results. Finally, in the concluding section the main points of this work are drawn and open problems are proposed.

II. MODEL

The proposed model represents a nonequilibrium reactive process taking place on a catalytic surface and involves re-

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action, adsorption and desorption steps. This model is used to describe the catalytic reduction of NO with H₂ on Pt lattice [14,15]. We assume that the catalytic surface is surrounded by a gas containing in excess NO and H₂ molecules with similar partial densities. A reaction between NO and H₂ takes place only on the surface of a catalyst (Pt) and after desorption of the products the catalytic site remains intact and can serve again. The model is described by the following chemical scheme:



where S represents an empty lattice site on the catalytic surface and the k_i 's are the corresponding constants of the reactions. The first equation describes the adsorption of a NO molecule on an empty site. If a neighboring empty lattice site is available, the NO molecule can be dissociated in two atoms N and O [Eq. (2)]. The dissociation probability has been measured in experiments and is of the order of 60% [16]. A hydrogen molecule can occupy an entire empty site because of its small size, Eq. (3). If an atomic oxygen and a hydrogen molecule are found in adjacent lattice sites they react forming a water molecule, which is desorbed from the catalytic surface leaving two empty lattice sites, as Eq. (4) indicates. Similarly, if two atomic nitrogens are found in adjacent lattice sites they react forming a nitrogen molecule that in turn desorbs from the catalytic surface leaving two empty lattice sites too, Eq. (5). These last two recombination/desorption processes have been modeled in one chemical reaction step in order to keep the system as simple as possible and to reduce the number of parameters involved.

A similar scheme may also describe the catalytic reduction of NO with CO, if H₂ is substituted by CO. Then the result of Eq. (4) will be the desorption of CO₂. Furthermore, because our proposed model does not involve any structural phase transitions of the catalytic surface it may provide a better description of the latter catalytic reduction [13]. In what follows we use the scheme of the NO+H₂ reaction, by considering cases where $1 \times 1 \rightleftharpoons \text{hex}$ phase transitions do not take place, and keeping in our mind the analogy with the NO+CO reduction.

In order to reduce further the parameters of our model we also treat the first two equations in one step. Then instead of Eqs. (1) and (2) we use the reaction



We assume that the constant k of the last reaction is equal to unity. That means that the remaining constants k_3 , k_4 , and k_5 are expressed in units of k . In the sequel we study the chemical system of Eqs. (6), (3), (4), and (5) on a two-dimensional square lattice, under the assumption $k=1$. Then the final system contains only three parameters: k_3 , k_4 , and k_5 .

III. MONTE CARLO SIMULATIONS

First we investigate the behavior of the system using Monte Carlo simulations on a square lattice consisting of $L \times L$ sites. We start with a completely empty lattice, where the appropriate reactions (6), (3), (4), or (5) take place randomly with corresponding probabilities

$$\frac{1}{\sum k}, \quad \frac{k_3}{\sum k}, \quad \frac{k_4}{\sum k}, \quad \text{and} \quad \frac{k_5}{\sum k},$$

respectively. The sum $\sum k$ in the denominators is defined as

$$\sum k = 1 + k_3 + k_4 + k_5,$$

for reasons of normalization. The simulations proceed via the following algorithm: (a) At each trial a random lattice site is chosen. (b) If this site is empty then with equal probability (50%) a molecule NO or H₂ will be found above the empty site [20]. In the former case, if also a neighboring lattice site is empty, then these sites can be substituted by N and O atoms with probability $1/\sum k$, otherwise there is no change. In the latter case H₂ will be deposited with probability $k_3/\sum k$. (c) If the randomly chosen lattice site is occupied by O, H₂ or N constituent, then the reactions (4) and (5) may take place with probabilities $k_4/\sum k$ and $k_5/\sum k$, respectively, provided that they have the right environment. (d) When a particular trial is finished we continue by choosing randomly another lattice site. (e) At each trial the time is equal to the total number of trials up until then, divided by the total number of lattice sites (L^2). That means that the unit of time considered is a Monte Carlo step, which is defined as L^2 trials. The temporal evolution of the concentration of each constituent is recorded.

The results of Monte Carlo simulations are summarized in Fig. 1. A square lattice of finite size, 40×40 sites, with periodic boundary conditions is used as a catalyst. Always the initial state is the empty lattice. As the simulation proceeds, after a period of some initial random fluctuations the system reaches a stationary state, where no activity exists. In this frozen, saturated state, there are no empty sites and the lattice is fully occupied by O, H₂ or N. Nevertheless the time t_o needed for reaching saturation and also the dominating constituent concentrations (H₂ or O) are strongly dependent on the kinetic parameters. For fixed values of k_4 and k_5 there exists a value of k_3 , denoted as k_3^{cr} , such that (a) for k_3 less than k_3^{cr} the atomic oxygen dominates in the lattice [see Fig. 1(a)], while (b) for k_3 greater than k_3^{cr} the lattice is finally mostly occupied by hydrogen [see Fig. 1(c)]. We call k_3^{cr} ,

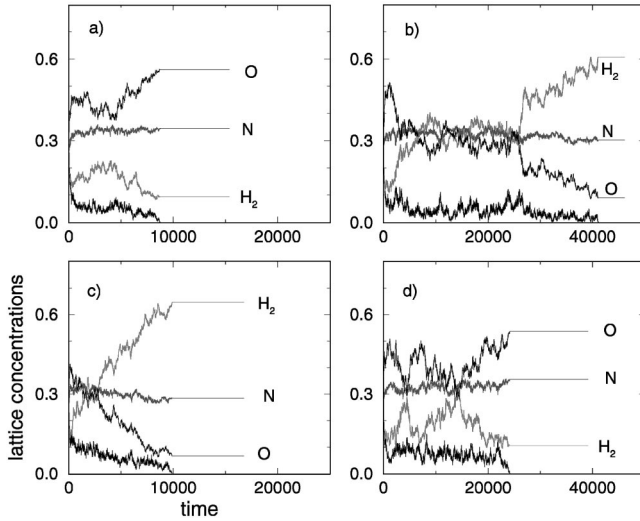


FIG. 1. Time evolution of the concentrations of sites covered by hydrogen (H_2), nitrogen (N), oxygen (O) and vacant sites on a 40×40 square lattice. The values of dimensionless reaction constants are $k_4=1$, $k_5=1$ and (a) $k_3=0.73$, (b) $k_3=0.74$, (c) $k_3=0.75$, and (d) $k_3=0.74$. The critical value is $k_3^{cr}=0.74$. Same random number sequence is used in cases (a), (b), (c) and different sequence in (d). The unit of time is a Monte Carlo step (1600 trials).

the ‘‘critical’’ value of k_3 , because it separates two domains of the parameter space with distinctive steady state concentrations. For the critical value k_3^{cr} the lattice reaches the saturated state after much longer times t_o , called also ‘‘saturation times,’’ where either the oxygen or the hydrogen dominates, depending on the random fluctuations in the particular simulation [see Figs. 1(b) and 1(d)]. In Fig. 1 the time evolution of the concentrations of H_2 , N, O, and vacant sites S are presented. In cases 1(a), 1(b), and 1(c) the time dependence of the concentrations are shown, for k_3 a slightly below, equal, and slightly above k_3^{cr} , respectively, using exactly the same sequence of random numbers. In case 1(d) a simulation using different random number sequence for k_3 equal k_3^{cr} is shown. In almost all the cases with k_3 near the critical value, the concentrations of the constituents at the frozen state are roughly as follows: the nitrogen is about 0.3, the dominating (O or H_2) about 0.6 and the third one (H_2 or O, respectively) about 0.1. There are no vacant sites at all in the frozen state. These approximately stationary concentrations near k_3^{cr} do not seem to be significantly affected from the variation of k_3 through its critical value. Only as we considerably depart from k_3^{cr} the concentration of the dominating constituent gradually increases at the expense of the other species’ concentrations.

The time t_o for the system to reach the frozen state shows a prominent maximum at the critical value k_3^{cr} . This can be seen in Fig. 2, where the mean value $\langle t_o \rangle$ with its statistical error is plotted as a function of parameter k_3 . The statistical mean value of t_o is calculated over twenty Monte Carlo simulations for the three values of k_3 round k_3^{cr} , because of large fluctuations of t_o near the critical value. This effect is normally called ‘‘critical slowing down.’’ Average over ten simulations are used for k_3 values away from criticality. We

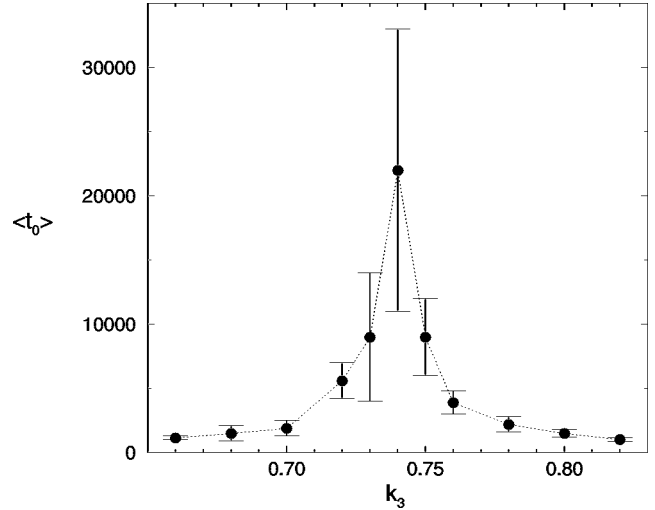


FIG. 2. The statistical mean value of time t_o needed by a 40×40 lattice for reaching the frozen state, as a function of parameter k_3 . The other parameters are $k_4=1$ and $k_5=1$. There is a prominent maximum at the critical value $k_3^{cr}=0.74$. Error bars represent statistical errors. The dotted line is a guide for the eye. The unit of time is a Monte Carlo step.

see from Fig. 2 that as we depart from the critical value, t_o drops very fast. For finite sizes there is a possibility at a particular simulation for k_3 equal to k_3^{cr} the time t_o to be smaller than the corresponding t_o of another simulation for k_3 slightly below or above of k_3^{cr} using different sequence of random numbers. However, for the same sequence of random numbers t_o is always larger at the critical value.

In Fig. 3 the dependence of k_3^{cr} on the parameters k_4 and k_5 is presented. In particular, the variation of k_3^{cr} as a function of k_4 is shown for three different values of k_5 differing from each other by one order of magnitude. In order to have a complete coverage of the parameter space k_4 is also varied over three orders of magnitude. As Fig. 3 shows, the

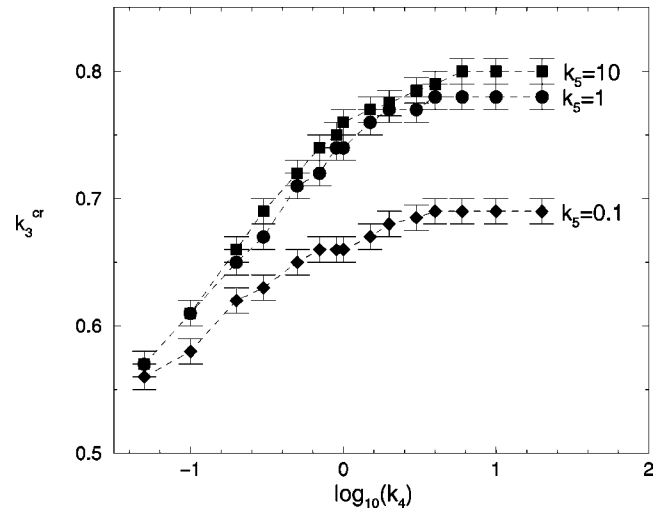


FIG. 3. The critical value k_3^{cr} as a function of $\log_{10}(k_4)$ for $k_5=0.1$ (diamonds), $k_5=1$ (circles), and $k_5=10$ (squares). The lattice size is 40×40 . The dashed lines are guides for the eye.

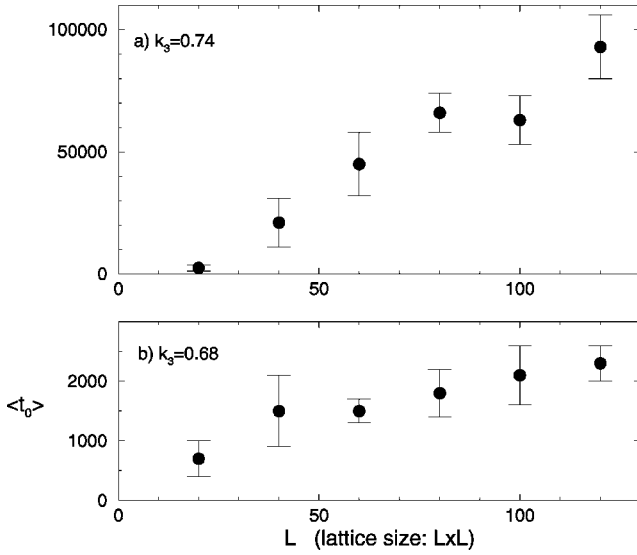


FIG. 4. The statistical mean value of time t_o needed by the system for reaching the frozen state, as a function of the linear dimension L of the lattice, for (a) $k_3 = k_3^{cr} = 0.74$ and (b) $k_3 = 0.68$. The lattice consists of $L \times L$ sites and the other parameters are $k_4 = 1$ and $k_5 = 1$. Error bars represent statistical errors. The unit of time is a Monte Carlo step (L^2 trials).

critical value k_3^{cr} is shifted to higher values for increasing k_4 and finally comes to a saturation value. The same behavior is observed when increasing k_5 . For small enough values of k_4 the value of k_3^{cr} only slightly depends on k_5 . As noted earlier, the surface of $k_3^{cr}(k_4, k_5)$ separates the three-dimensional parameter space (k_3, k_4, k_5) in two qualitatively different areas. Above (below) this surface the hydrogen (oxygen) dominates in the lattice when the frozen state is reached. For values of parameters lying on this surface the finite size catalyst remains active for much longer times.

Finally, the dependence of the characteristic time t_o needed for the system to reach the frozen state is studied as a function of the lattice size $L \times L$. Figure 4 shows the mean value $\langle t_o \rangle$ calculated over ten Monte Carlo runs, as a function of L . The error bars represent statistical errors. In Fig. 4(a) this calculation is presented for the critical value k_3^{cr} , while in Fig. 4(b) for a value of $k_3 \neq k_3^{cr}$. Notice the difference in the time scales between these two plots. We see that $\langle t_o \rangle$ increases more abruptly with the lattice size at the critical value. For example, the ratio of $\langle t_o \rangle$ for lattice 120×120 to the corresponding $\langle t_o \rangle$ for lattice 20×20 is ten times larger in Fig. 4(a) ($k_3 = k_3^{cr}$) compared to Fig. 4(b) ($k_3 \neq k_3^{cr}$). This suggests that the activity on a macroscopic catalyst lasts for much longer times when the reactive constants are at criticality.

IV. MEAN-FIELD APPROXIMATION

In the mean-field approximation the concentrations x_S , x_N , x_O , and x_H of the constituents of the chemical system described by Eqs. (6), (3), (4), and (5) obey the following equations:

$$\frac{dx_S}{dt} = -2x_S^2 - k_3x_S + 2k_4x_Ox_H + 2k_5x_N^2, \quad (7)$$

$$\frac{dx_N}{dt} = x_S^2 - 2k_5x_N^2, \quad (8)$$

$$\frac{dx_O}{dt} = x_S^2 - k_4x_Ox_H, \quad (9)$$

$$\frac{dx_H}{dt} = k_3x_S - k_4x_Ox_H, \quad (10)$$

where, as before, we have assumed that $k = 1$. Taking into account that

$$x_S + x_N + x_O + x_H = 1, \quad (11)$$

we can substitute x_H at the previous equations to obtain the dynamical system

$$\begin{aligned} \frac{dx_S}{dt} = & -2x_S^2 - k_3x_S + 2k_4x_O - 2k_4x_Ox_S - 2k_4x_Ox_N - 2k_4x_O^2 \\ & + 2k_5x_N^2, \end{aligned} \quad (12)$$

$$\frac{dx_N}{dt} = x_S^2 - 2k_5x_N^2, \quad (13)$$

$$\frac{dx_O}{dt} = x_S^2 - k_4x_O + k_4x_Ox_S + k_4x_Ox_N + k_4x_O^2. \quad (14)$$

This system has the following two trivial fixed points:

$$P_1: \quad x_S = 0, \quad x_N = 0, \quad x_O = 0 \quad (\Rightarrow x_H = 1), \quad (15)$$

$$P_2: \quad x_S = 0, \quad x_N = 0, \quad x_O = 1 \quad (\Rightarrow x_H = 0). \quad (16)$$

Linear stability analysis shows that the P_1 fixed point, given by Eq. (15), is stable. The eigenvalues of the linear stability matrix at P_1 are

$$0, \quad -k_3, \quad \text{and} \quad -k_4.$$

The fixed point P_2 , given by Eq. (16), is unstable. The corresponding eigenvalues are

$$0, \quad \text{and} \quad \frac{-(k_3 + k_4) \pm \sqrt{(k_3 + k_4)^2 + 4k_3k_4}}{2}.$$

A saddle-node bifurcation takes place in the dynamical system and two nontrivial fixed points appear. For fixed values of the parameters k_3 and k_5 the bifurcation point for k_4 is

$$k_4^{cr} = \frac{8k_3^2k_5}{[k_3(1 + \sqrt{2k_5}) - \sqrt{2k_5}]^2}. \quad (17)$$

For $k_4 \geq k_4^{cr}$ the additional fixed points are given by

$$P_3: \quad x_S = k_3, \quad x_N = \frac{k_3}{\sqrt{2k_5}}, \quad x_O = y_+, \quad (18)$$

$$P_4: \quad x_S = k_3, \quad x_N = \frac{k_3}{\sqrt{2k_5}}, \quad x_O = y_-, \quad (19)$$

where

$$y_{\pm} = \frac{1}{2} \left(1 - k_3 \frac{1 + \sqrt{2k_5}}{\sqrt{2k_5}} \right) \pm \frac{1}{2} \sqrt{\frac{k_4 [k_3 (1 + \sqrt{2k_5}) - \sqrt{2k_5}]^2 - 8k_3^2 k_5}{2k_4 k_5}}. \quad (20)$$

If the condition

$$k_3 < \frac{\sqrt{2k_5}}{1 + \sqrt{2k_5}} \quad (21)$$

holds (and under the bifurcation condition $k_4 \geq k_4^{cr}$), then the concentrations x_S , x_N , and x_O given by Eqs. (18) and (19) belong in the proper area from 0 to 1. The stable fixed point is P_3 , given by Eq. (18). Since

$$y_+ + y_- = 1 - k_3 - \frac{k_3}{\sqrt{2k_5}} = 1 - x_S - x_N = x_O + x_H, \quad (22)$$

for the stable node solution we have $x_O = y_+$ and consequently $x_H = y_-$. That means that the dependence of the concentrations x_O and x_H on k_4 is very simple, and is given by the variation of y_+ and y_- , respectively. For $k_4 = k_4^{cr}$ there are equal concentrations $x_O = x_H = \frac{1}{2}(1 - x_S - x_N)$. As k_4 increases the oxygen (hydrogen) stationary concentration is gradually increased (decreased) up to its limiting value $1 - x_S - x_N$ (zero) for $k_4 \rightarrow \infty$.

The system of Eqs. (12)–(14) was solved numerically under the restriction of Eq. (21), using as initial condition: $x_S = 1$, $x_N = 0$, $x_O = 0$. Then for k_4 less than k_4^{cr} the system goes to the trivial stable fixed point P_1 , Eq. (15), while for k_4 greater than k_4^{cr} the system reaches the equilibrium P_3 , Eq. (18). It is observed that under the restriction of the condition (21) the surface at the parameter space defined by Eq. (17) plays the same role as that of Fig. 3 discussed in the previous section, i.e., defines the limits of the dominating constituent in the competition between oxygen and hydrogen. The case k_4 less (greater) than k_4^{cr} corresponds to k_3 greater (less) than k_3^{cr} , where hydrogen (oxygen) dominates at the stationary state of the system. Moreover, the activity on the catalyst remains for much larger times when the parameters lie on the critical surface. In Fig. 5 the solid lines show projections of this surface on the two-dimensional plane of k_3 and k_4 for three different values of k_5 at 0.1, 1, and 10, respectively, as given by Eq. (17). The results of Fig. 3 (with the error bars) are also included for comparison with Monte Carlo simulations.

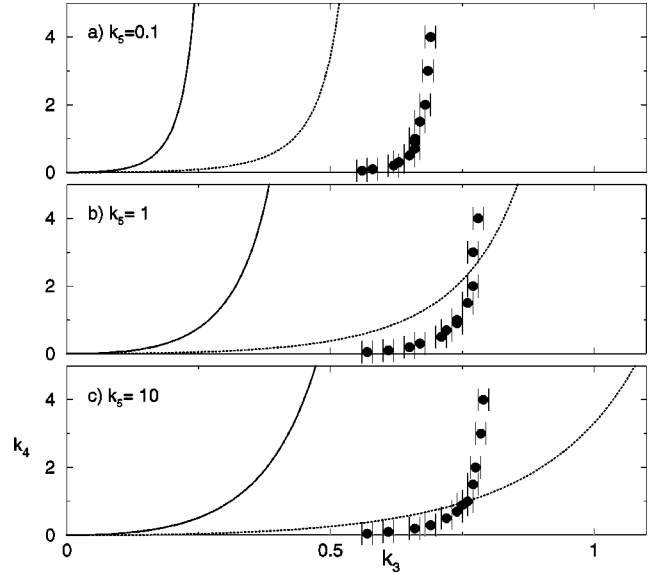


FIG. 5. Projections of the critical surface on parameter space in the plane of k_3 and k_4 , for (a) $k_5 = 0.1$, (b) $k_5 = 1$, and (c) $k_5 = 10$. Solid lines show the results of the mean-field approximation, Eq. (17). Dotted lines represent the results of the improved mean-field approximation, Eq. (37). The data of Fig. 3 are also added for comparison with Monte Carlo simulations.

Beyond the quantitative disagreement between the mean field predicted and the Monte Carlo calculated critical surface, depicted in Fig. 5, there are also further differences at the semiquantitative level. In particular, in the domain of hydrogen domination the mean-field equilibrium is characterized by the absence not only of vacant sites (as in Monte Carlo simulations) but also of nitrogen and oxygen. The system is fully covered by hydrogen in disagreement with the situation depicted in Fig. 1(c), where nitrogen and oxygen are also present at the frozen state. At the other side of the critical surface the vacant site concentration is nonzero in the mean-field approximation [Eq. (18)], which does not happen in Fig. 1(a). Furthermore, although the oxygen concentration is greater than hydrogen, this is not necessarily valid in comparison with nitrogen or vacant sites concentrations.

We can conclude that the mean-field approximation predicts the existence of the critical surface and its main role in the qualitative behavior of the system, although it cannot reproduce accurately in quantitative level the results of Monte Carlo simulations. This success is very important provided that mean field is a very crude approximation that does not take into account basic properties of the catalytic surface such as the discreteness of the lattice and its two-dimensional character.

V. IMPROVED MEAN FIELD APPROXIMATION

We are able to improve quantitatively the results of the mean-field approximation, by using as a starting point a discrete version of Eqs. (7)–(10), which better match the nature of the catalyst. To assimilate the Monte Carlo rules we consider explicitly the spatial arrangement of the reactants and products. For this purpose we introduce for each lattice site i

the corresponding site probabilities N_i , O_i , H_i , and S_i to find a nitrogen, oxygen, hydrogen, or a vacant site respectively. Obviously we have

$$N_i + O_i + H_i + S_i = 1 \quad \text{for each lattice site } i. \quad (23)$$

The full state of the system can be described by the time-dependent probability distribution function $P(\{\sigma_i\}, t)$, where each spinlike variable σ_i represents any of the four possible states (N, O, H, S) of site i . For the two-dimensional square lattice catalyst the index i takes values $i=1, 2, \dots, L \times L$. The evolution of the probability distribution is described by the Master equation [10,21,22]

$$\begin{aligned} \frac{\partial P(\{\sigma_i\}, t)}{\partial t} = & - \sum_j w_j(\{\sigma_i\} \rightarrow \{\sigma'_i\}) P(\{\sigma_i\}, t) \\ & + \sum_j w_j(\{\sigma'_i\} \rightarrow \{\sigma_i\}) P(\{\sigma'_i\}, t). \end{aligned} \quad (24)$$

The transition probabilities $w_j(\{\sigma'_i\} \rightarrow \{\sigma_i\})$ represent the transition from state $\{\sigma'_i\}$ to state $\{\sigma_i\}$. During the evolution only one of the lattice sites changes at a time and the transition rates w_j depend on the state of the four neighbor sites. For example, site j being currently on state N (nitrogen covered) can change into state S (empty site) provided that any of the neighbors is at the state N and the transition probability is then proportional to the reaction rate k_5 . The probability S_i of a given site i to be on a state S (and similarly for all other constituents) can be written in terms of the global probability distribution:

$$S_i(t) = \sum_{\sigma_j, j \neq i} P(\sigma_1, \sigma_2, \dots, \sigma_i = S, \sigma_{i+1}, \dots, \sigma_{L \times L}, t). \quad (25)$$

Using Eqs. (24) and (25) we can find the evolution equation for the site probability S_i . However, the equation includes terms proportional to the two-site probability $S_{i,i+\delta}$ to find simultaneously S particles both on sites i and $i+\delta$. By truncating these terms into $S_{i,i+\delta} = S_i S_{i+\delta}$ we find the first order truncated equations as:

$$\begin{aligned} \frac{dS_i}{dt} = & -k \sum_{\delta} S_i S_{i+\delta} - k_3 S_i + k_5 \sum_{\delta} N_i N_{i+\delta} \\ & + k_4 \sum_{\delta} (O_i H_{i+\delta} + H_i O_{i+\delta}), \end{aligned} \quad (26)$$

$$\frac{dN_i}{dt} = \frac{1}{2} k \sum_{\delta} S_i S_{i+\delta} - k_5 \sum_{\delta} N_i N_{i+\delta}, \quad (27)$$

$$\frac{dO_i}{dt} = \frac{1}{2} k \sum_{\delta} S_i S_{i+\delta} - k_4 \sum_{\delta} O_i H_{i+\delta}, \quad (28)$$

$$\frac{dH_i}{dt} = k_3 S_i - k_4 \sum_{\delta} H_i O_{i+\delta}, \quad (29)$$

where the \sum_{δ} indicates summation over all the first neighbors of the lattice site i . The factors in expressions (26)–(29) arise from the need to change the state of the given site i , and not the state of the entire system, as is the case of the mean field. For a two-dimensional rectangular lattice, such as the catalytic surface that is considered here, each summation \sum_{δ} contains four terms. Using the conservation of probability, given by Eq. (23), we can solve for H_i (for example) and substitute it in Eqs. (26)–(28). Then, for a lattice of $L \times L$ sites, we need to solve a system of $3L^2$ coupled equations for calculating the local densities $S_i(t)$, $N_i(t)$, and $O_i(t)$. This system constitutes the discrete version of the mean-field approximation. Instead of three, we now deal with $3L^2$ nonlinear first order differential equations. This way one takes explicitly into account the discrete nature and the two-dimensional character of the catalyst. The total concentrations of each constituent are given at any time by the relations:

$$\begin{aligned} N(t) &= \frac{1}{L^2} \sum_i N_i(t), \quad O(t) = \frac{1}{L^2} \sum_i O_i(t), \\ S(t) &= \frac{1}{L^2} \sum_i S_i(t) \end{aligned} \quad (30)$$

and

$$H(t) = 1 - N(t) - O(t) - S(t). \quad (31)$$

The complicated discrete system of Eqs. (26)–(29) may be simplified if we consider an homogeneous initial condition, where all the probabilities for $t=0$ are site independent, i.e., $S_i(0) = x_S(0)$, $N_i(0) = x_N(0)$, $O_i(0) = x_O(0)$, and $H_i(0) = x_H(0)$ for each site i . Then we observe from the equations of motion that the time derivatives of each constituent are also independent of the particular site, leading to common time evolution of the probabilities of every constituent at each lattice site, i.e.,

$$\begin{aligned} S_i(t) &= x_S(t), \quad N_i(t) = x_N(t), \quad O_i(t) = x_O(t) \\ \text{and } H_i(t) &= x_H(t), \quad \text{for each site } i. \end{aligned} \quad (32)$$

In that case the discrete system is reduced to a simple one of the standard mean-field type. Taking into account that each sum \sum_{δ} merely contributes a factor of 4, putting $k=1$ as previously, dividing by a factor of 2 each one of the four remaining equations and rescaling also by 2 the time (i.e., considering $\tau=2t$), we finally obtain the reduced mean-field system:

$$\frac{dx_S}{d\tau} = -2x_S^2 - \frac{k_3}{2} x_S + 2k_5 x_N^2 + 4k_4 x_O x_H, \quad (33)$$

$$\frac{dx_N}{d\tau} = x_S^2 - 2k_5 x_N^2, \quad (34)$$

$$\frac{dx_O}{d\tau} = x_S^2 - 2k_4 x_O x_H, \quad (35)$$

$$\frac{dx_H}{d\tau} = \frac{k_3}{2} x_S - 2k_4 x_O x_H. \quad (36)$$

Comparing the resulting system with the standard mean-field system of Eqs. (7)–(10) we conclude that for homogeneous initial conditions the only effect of the discrete two-dimensional nature of the catalytic surface in the mean-field approximation, besides time rescaling, is the renormalization of the two constants of reactions k_3 and k_4 to values $k_3/2$ and $2k_4$, respectively. Consequently all the discussion and the results of the previous section are valid exactly, if we merely substitute the parameters k_3 and k_4 by their renormalized values. As a result, from Eq. (17) we obtain that the critical surface, in the improved mean-field approximation described here, is given by

$$k_4^{cr} = \frac{k_3^2 k_5}{\left[\frac{k_3}{2} (1 + \sqrt{2k_5}) - \sqrt{2k_5} \right]^2}. \quad (37)$$

In Fig. 5 we plot with dotted lines the intersections of the critical surface given by Eq. (37), with the planes $k_5 = 0.1, 1, \text{ and } 10$, respectively. Comparing with the Eq. (17) arising from the standard mean-field approximation we conclude that the renormalization, coming from the homogeneous discrete system, significantly improves the quantitative agreement of the theoretical mean-field results with the data of the Monte Carlo simulations (Fig. 5, circles). Especially in the case where all the reaction constants are of about the same order of magnitude, the agreement is considerably better [see Fig. 5(b)]. In almost all cases the improved mean-field equations approximate better the Monte Carlo results, except for the case where the k_5 and k_4 are much larger than k_3 . Furthermore, at equilibrium, in the range of parameters where oxygen dominates (for k_4 greater than k_4^{cr}), the concentration of vacant sites is decreased from k_3 to $k_3/2$ [see Eq. (18)], reducing by half its difference from zero, i.e., the corresponding Monte Carlo equilibrium value [see Fig. 1(a)].

Consequently, the improved mean-field approximation that effectively leads to a renormalization of the values of the reaction constants by taking into account more detailed information of the surface lattice structure of the catalyst [23], is able to reproduce more accurately the results of Monte Carlo simulations. Further models, taking into account random local fluctuations, are expected to give more realistic results closer to the Monte Carlo results.

VI. CONCLUSIONS

Catalytic reactions restricted on two-dimensional supports present a rich spatiotemporal behavior that cannot always be well described by the standard mean-field models. As a working example we have studied the catalytic reduction of NO and H₂ (or CO) on a Pt lattice. This process is described by a minimal set of chemical reactions [Eqs. (6), (3)–(5)], using three reaction constants as parameters. Monte Carlo simulations, starting with a completely empty square lattice, showed that after a period of some random fluctuations the

system comes to a stationary, frozen, fully covered state. The time needed for the system to reach the equilibrium state depends on the parameter values and on the lattice features. A critical surface exists in the parameter space, which divides the parameter space in two domains where either the oxygen or the hydrogen dominates at the stationary state of the lattice. On the dividing critical surface the catalyst remains active (unsaturated) for longer times, comparative to the saturation times calculated for parameters outside the critical surface. We also examined the dependence of the saturation time on the lattice size. As expected, the corresponding time increases abruptly for parameter values around the critical surface.

In the framework of the standard mean-field approximation the stationary states of the chemical system are described by stable fixed points of the corresponding dynamical system. A saddle-node bifurcation takes place providing the critical surface of the long time activity, which also defines the limits of the dominating constituent in the competition between hydrogen and oxygen. This bifurcation predicts only the qualitative features of the system. The apparent qualitative success of the mean field results in our simplified system may be related with the simple evolution of the reactant coverages towards the trivial poisoning state. However, this approximation should not be appropriate for describing richer models with more complex behavior, that are possibly able to account for experimentally observed spatiotemporal self-organized patterns [24,25].

To improve agreement with Monte Carlo simulations at the quantitative level, it is necessary to explicitly consider the discrete, two-dimensional character of the catalytic surface. For homogeneous initial conditions the discrete set of coupled differential equations leads to an improved mean-field scheme, which, through a renormalization of the reaction constants, gives analytical results in better quantitative agreement with those obtained from Monte Carlo simulations and a better representation of the critical surface.

In a real catalytic reduction there are at least two physical mechanisms present that are not taken into account in this description and tend to raise the poisoning that always appears in our simulations. The first one is the desorption of NO and H₂ (or CO) taking place above 400 K [14], which creates vacant sites and accelerates the reaction. This seems to be responsible for the “surface explosion” and the chemical oscillations observed in the experiments [14–16]. Another mechanism is the reaction between next nearest-neighbor reactants. We have considered that the reactions (4) and (5) may occur only whenever the reactants occupy adjacent sites in the square catalytic surface. The frozen states that appear in the Monte Carlo simulations consist of islands of oxygens or hydrogens that are surrounded by nitrogens arranged in second neighboring sites among themselves, forming a closed contour. As a result, if we allow the reactions (4) and (5) to take place between second neighbors with smaller probabilities compared to first neighboring reactants, there will be a sustained activity at least near the critical surface. Both these mechanisms are currently under consideration [26].

As explained in the introduction this minimal model does not address the problem of oscillatory chemical kinetics and surface phase transition observed for certain temperature ranges in surface catalysis. To account for these effects multimolecular auto-catalytic steps need to be included into the model [27]. These will introduce higher order nonlinearities within the mean-field equations that in turn can give rise to multistability, sustained oscillations, and pattern formation. In addition, diffusion effects that will homogenize the system and that are known to contribute in the establishment of oscillatory regimes need also to be considered in a realistic

representation of a catalytic process. All these details can be incorporated in the current model, both in the mean-field approaches and in the Monte Carlo scheme, and predict a much richer spatiotemporal behavior, including pattern formations and nonequilibrium, oscillatory steady states.

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