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Monte Carlo simulations of oscillations

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Abstract

Results of Monte Carlo simulations of CO oxidation with site blocking, and of the Lotka model ($A(\text{gas}) \rightarrow A(\text{ads})$, $B(\text{ads}) \rightarrow B(\text{gas})$, $A(\text{ads}) + B(\text{ads}) \rightarrow 2B(\text{ads})$) are presented. The introduction of a site blocking adsorbate can lead to oscillations in CO oxidation. The system is bistable for certain coverages of the site blocking adsorbate; adsorption and desorption of that adsorbate drive the system from one stable state to the other and back. The oscillations in the Lotka model are due to avalanches of A's that are converted into B's by the autocatalytic step. Normal rate equations are unable to describe these systems correctly.

Keywords: Monte Carlo; Lattice–gas model; Oscillatory reactions

1. Introduction

Reactions on surfaces of catalysts generally involve adsorbates that are adsorbed on neighboring sites. The kinetics depends therefore on the correlation in the occupation of neighboring sites. This correlation is affected by lateral interactions [1–3], but also by high reaction rates [4,5]. For example, a fast reaction between two adsorbates will lead to segregation, because in the region where they meet they will react away. A good theory of kinetics of catalysis should take this correlation in the occupation of sites into account.

In this paper I present a method with which it is possible to simulate how the occupation of all sites of a catalyst's surface changes over a long

period of time. A lattice–gas model is used to represent the catalyst's surface, and the evolution of the adlayer is described by a master equation that is solved numerically via a Monte Carlo simulation. The master equation contains so-called transition probabilities. These can be determined by fitting to experimental data, but one can also try to calculate them ab initio, very similarly to the calculations of rate constants that have been published recently [6,7].

The kinetics of reactions on surfaces is usually described in terms of macroscopic rate equations that indicate how the coverages of the adsorbates change in time [8,9]. These equations can be derived from the master equation, but this involves some approximations that need not be correct. The term anomalous kinetics has been used to describe the inadequacy of the macroscopic rate equations [10].

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I present results of Monte Carlo simulations for two systems that show oscillations. Oscillatory reaction on catalysts draw currently a lot of attention, mainly because of the work in the groups of Ertl and King on CO oxidation [11,12]. Oscillations pose an interesting problem for Monte Carlo simulations. It is quite common that an oscillation can be observed on some small part of the catalyst. Different parts may oscillate out-of-phase, however, and the net result is that there is no global oscillation. A synchronization mechanism is needed to prevent the adlayer splitting up into out-of-phase local oscillations. It is interesting that such a mechanism can result from only short-range interactions, and Monte Carlo simulations show how such mechanism operates on an atomic scale. The two systems also clearly show the shortcomings of macroscopic rate equations.

2. Theory

One can take into account the effect of the occupation of the neighboring sites on the reactivity of adsorbates by describing the evolution of the adlayer with a master equation [13]

$$\frac{dP_{\{s_i\}}}{dt} = \sum_{\{s'_i\}} [W_{\{s_i\}\{s'_i\}} P_{\{s'_i\}} - W_{\{s'_i\}\{s_i\}} P_{\{s_i\}}], \quad (1)$$

where $\{s_i\}$ and $\{s'_i\}$ refer to the configuration of the adlayer (i.e., s_i and s'_i are the adsorbates at site i before and after a reaction), the P 's are the probabilities of the configurations, t is time, and the W 's are transition probabilities per unit time. These transition probabilities give the rates with which reactions change the occupations of the sites. The number of relevant transition probabilities is limited; $W_{\{s'_i\}\{s_i\}} = 0$ when more than a few s'_i 's differ from the s_i 's, because each reaction changes only the occupation of a few sites. Many transition probabilities are also equal to each other; all configuration changes caused by a particular type of reaction have the same W .

The master equation bridges the gap between first principles and macroscopic rate equations. The link to first principles is made by expressions for the transition probabilities. These can be obtained in almost the same way as expressions for rate constants in variational transition-state theory [14–16]. The difference is in the partitioning of the phase space of the system. In variational transition-state theory one defines only one dividing surface that splits phase space in a region corresponding to reactants and one corresponding to products. Here phase space is split into many regions, each of which corresponds to a particular configuration of the adlayer. The transition probability $W_{\{s'_i\}\{s_i\}}$ for the reaction that changes the adlayer from $\{s_i\}$ to $\{s'_i\}$, is then given by the flux through the dividing surface that separates the corresponding regions in phase space divided by the probability to find the system in the region corresponding to $\{s_i\}$ (see Fig. 1). This rather abstract formulation reduces to

$$W_{\{s'_i\}\{s_i\}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} e^{-E_{\text{bar}}/k_B T}, \quad (2)$$

an expression which is well-known from transi-

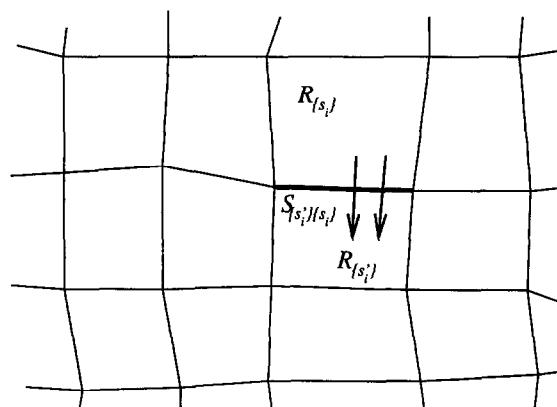


Fig. 1. Schematic drawing of the partitioning of phase space into regions R , each of which corresponds to some particular configuration of the adlayer. The reaction that changes $\{s_i\}$ into $\{s'_i\}$ corresponds to a flow from $R_{\{s_i\}}$ to $R_{\{s'_i\}}$. The transition probability $W_{\{s'_i\}\{s_i\}}$ for this reaction equals the flux through the surface $S_{\{s'_i\}\{s_i\}}$ separating $R_{\{s_i\}}$ from $R_{\{s'_i\}}$, divided by the probability to find the system in $R_{\{s_i\}}$.

tion-state theory [8,9]. However, one should keep in mind that this is a rigorous expression for the master equation, but not for macroscopic rate equations. In principle, this equation can be used in ab-initio calculations of the transition probabilities.

Macroscopic rate equations can be derived from the master equations. I would like to give two examples to illustrate the method, and to show what approximations may have to be used. Suppose there is only one type of adsorbate, say A, which desorbs. The coverage θ_A is defined as an ensemble average

$$\theta_A = \frac{1}{S} \sum_{\{s_i\}} P_{\{s_i\}}(A)_{\{s_i\}}, \quad (3)$$

where S is the number of sites, and $(A)_{\{s_i\}}$ is the number of A's in configuration $\{s_i\}$ (i.e.; the number of s_i equal to A). This leads to

$$\begin{aligned} \frac{d\theta_A}{dt} &= \frac{1}{S} \sum_{\{s_i\}} \frac{dP_{\{s_i\}}}{dt} (A)_{\{s_i\}} \\ &= \frac{1}{S} \sum_{\{s_i\}\{s'_i\}} W_{\{s_i\}\{s'_i\}} P_{\{s'_i\}} [(A)_{\{s_i\}} - (A)_{\{s'_i\}}] \\ &= -\frac{1}{S} W_{\text{des}}^{(1)} \sum_{\{s'_i\}} P_{\{s'_i\}} (A)_{\{s'_i\}} \\ &= -W_{\text{des}}^{(1)} \theta_A. \end{aligned} \quad (4)$$

Desorption reduces the number of A's by one, so that $W_{\{s_i\}\{s'_i\}} \neq 0$ only if all s_i are the same as the s'_i except for the site with a desorbing A. Therefore for each $\{s'_i\}$ the number of non-vanishing terms in the summation over $\{s_i\}$ equals $(A)_{\{s'_i\}}$, and for each of these terms we have $W_{\{s_i\}\{s'_i\}} = W_{\text{des}}^{(1)}$ (no lateral interactions), and $(A)_{\{s_i\}} = (A)_{\{s'_i\}} - 1$. This explains the third step of the derivation. Note that the expression above is exact.

Suppose now that the desorption is associative for neighboring adsorbates ($2A(\text{ads}) \rightarrow A_2(\text{gas})$). The first two steps of Eq. (4) still hold. Now $(A)_{\{s_i\}} = (A)_{\{s'_i\}} - 2$ must hold, and the number of new configurations that can result from desorption of a pair of A's equals the

number of neighboring pairs in the current configuration; i.e.,

$$\frac{d\theta_A}{dt} = -\frac{2}{S} W_{\text{des}}^{(2)} \sum_{\{s'_i\}} P_{\{s'_i\}} (AA)_{\{s'_i\}}, \quad (5)$$

where $(AA)_{\{s'_i\}}$ is the number of pairs of neighboring A's in configuration $\{s'_i\}$. This is still an exact expression, but to reduce it to the familiar expression in terms of θ_A two approximations have to be made. First, the A's are assumed to be randomly distributed. This means

$$(AA)_{\{s'_i\}} = \frac{Z}{2S} (A)_{\{s'_i\}}^2, \quad (6)$$

where Z is the coordination number. Second, the fluctuations in the coverage are assumed to be negligible; i.e.,

$$\sum_{\{s'_i\}} P_{\{s'_i\}} (A)_{\{s'_i\}}^2 = \left[\sum_{\{s'_i\}} P_{\{s'_i\}} (A)_{\{s'_i\}} \right]^2. \quad (7)$$

The final expression is then

$$\frac{d\theta_A}{dt} = -ZW_{\text{des}}^{(2)} \theta_A^2. \quad (8)$$

The second approximation becomes exact in the thermodynamic limit [13], but the first one need not be a good approximation at all. In that case there does not seem to be a justification to use macroscopic rate equations. A situation where the first approximation seems to be a good one is when there is fast diffusion (however, see Ref. [17]). Note also the appearance of the coordination number in the rate equation.

Although the master equation can formally be solved, this is in general not practical, because of the extremely large number of possible configurations of the adlayer. Instead one uses a Monte Carlo procedure. There are a number of Monte Carlo methods to simulate the evolution of an adlayer [2,18–21]. The following seems to be the most efficient one for the systems I will discuss below. The adlayer evolves through a series of reactions, and time is incremented after each reaction. The method to determine the

reaction and the corresponding time increment consists of three steps. Let's assume that at time t the adlayer is in configuration $\{s_i\}$. Then first determine the time $t + \Delta t$ at which the next reaction will take place. This time is given by

$$\Delta t = -\frac{\ln r}{\sum_{\{s_i\}} W_{\{s_i\}}}, \quad (9)$$

where r is a uniform deviate $0 < r \leq 1$. The denominator is the total rate of change for configuration $\{s_i\}$. Next determine the *type* of reaction k (desorption, adsorption, dissociation, etc.) that will take place. This is given by

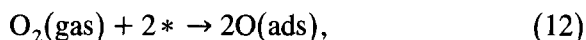
$$\frac{\sum_{l=1}^{k-1} N_l W_l}{\sum_{l=1}^{N_{\text{type}}} N_l W_l} < r' \leq \frac{\sum_{l=1}^k N_l W_l}{\sum_{l=1}^{N_{\text{type}}} N_l W_l}, \quad (10)$$

with r' another uniform deviate $0 < r' \leq 1$, N_l the number of possible reactions of type l , W_l the corresponding transition probability, and N_{type} the number of reaction types. Finally, determine where that reaction takes place. This can be done by randomly picking sites until one has been found where the reaction is possible. The computer time per reaction for this method does not depend on the system size. It can be shown that it generates configurations with the correct probabilities. For the Lotka model (see below) the last step can be done even more efficiently by making lists of the vacant sites and of the sites with a B adsorbate. Adsorption of A and desorption of B can then be done by simply picking a random element of one of these lists.

3. Results and discussions

The two models that I will discuss in this section both show oscillations. Mathematically oscillations result from the existence of a limit cycle in some phase space of the system [22,23]. (The term phase space is used here as the space spanned by some properties, like coverages, that characterize the system.) However, there may be various chemical mechanisms leading to a limit cycle, as will be illustrated below.

A large number of Monte Carlo studies have been published using the Ziff–Gulari–Barshad model (ZGB-model) of CO oxidation [21]. This model contains just three reactions.



Here $*$ means a vacant sites, and the sites in the last two reactions are nearest neighbors. The

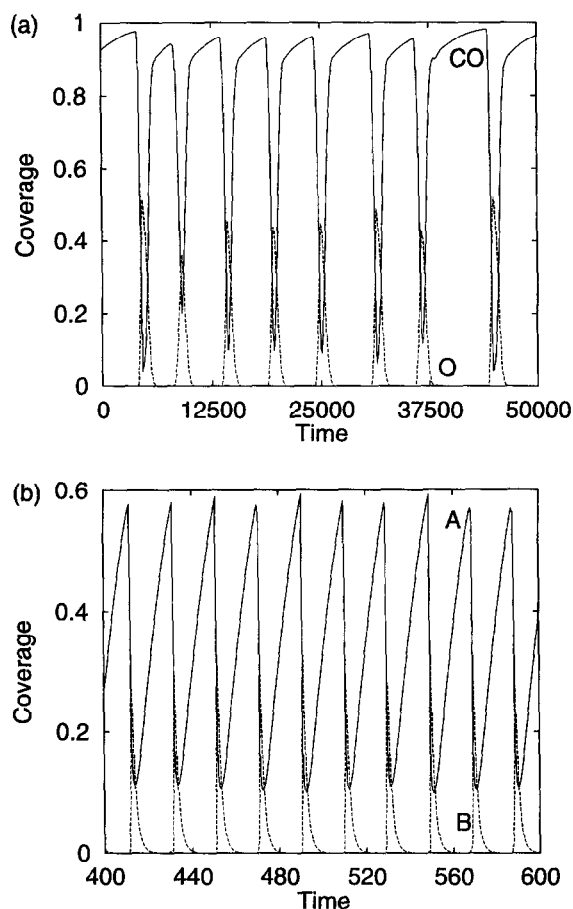


Fig. 2. Temporal variations of θ_{CO} and θ_{O} in CO oxidation with site blocking (a), and of θ_{A} and θ_{B} in the Lotka model (b). The former has been obtained from a simulation on a 256×256 square grid with transition probabilities 1 for CO adsorption, 0.52 for O_2 adsorption, 0.001 for CO desorption, 0.0003 for X adsorption and desorption, and infinitely fast CO_2 formation. The latter has been obtained from a simulation on a 2048×2048 square grid with transition probabilities 0.05 for A adsorption, 0.95 for B desorption, and infinitely fast autocatalytic step.

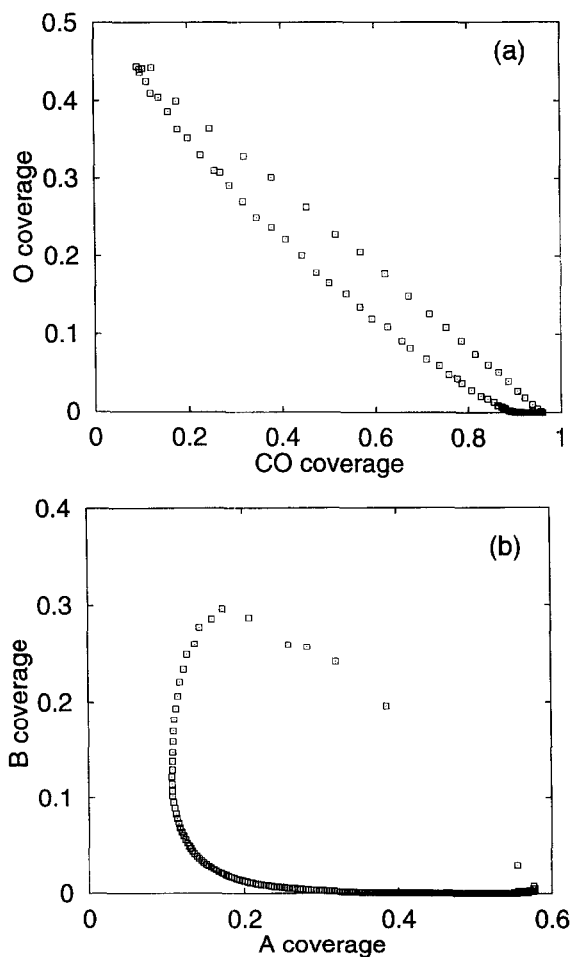


Fig. 3. Trajectories in the (θ_{CO}, θ_O) -plane for CO oxidation with site blocking (a), and in the (θ_A, θ_B) -plane for the Lotka model (b) representing one typical period of the oscillations in each case. The same simulations have been used as for Fig. 2. The dots in (a) are 30 time units apart, and in (b) 0.1 time units. The systems move anti-clockwise.

formation of CO_2 is assumed to be infinitely fast.

The ZGB-model does not show oscillations, but it does show kinetic phase transitions; a second-order one from a reactive (i.e., CO_2 -producing) state to a state where the surface is completely covered by oxygen (O-poisoning), and a first-order one from the reactive state to a state where the surface is completely covered by CO (CO-poisoning). As has been observed first by Eigenberger, one can obtain oscillations by

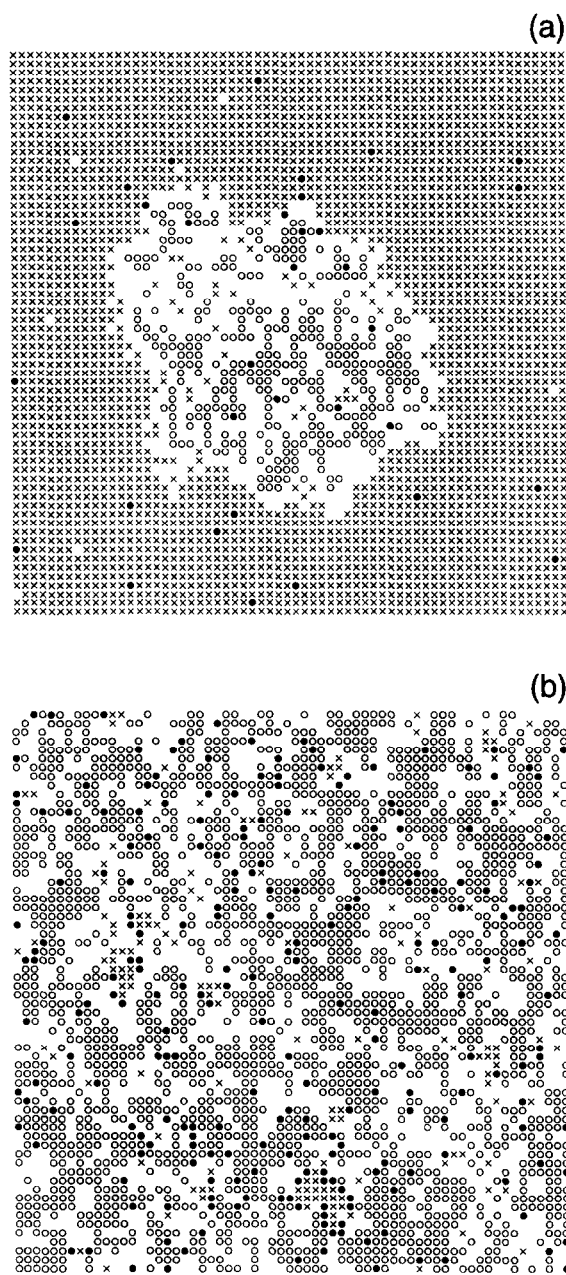
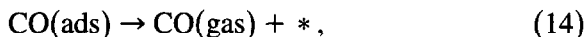


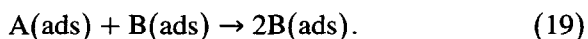
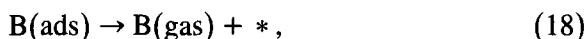
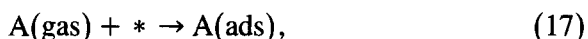
Fig. 4. Snapshots of the adlayer at different moments during one cycle of the oscillations of CO oxidation with site blocking obtained from a simulation with a 64×64 square grid. The CO molecules are depicted by crosses, open circles are oxygen atoms, and closed circles depict the site blocking adsorbate. The transition from the CO-poisoned to the reactive state is shown in (a), and the reactive state is shown in (b). Transition probabilities are as for Fig. 2.

introducing a site blocking mechanism [24,25]. For the ZGB-model this can be done by adding



CO desorption is necessary to avoid trapping the system in the CO-poisoned state. The last two reactions are slow, and the only function of X is to block sites. Models have been proposed to explain oscillations in CO oxidation where X is unreactive CO, subsurface oxygen, or carbon formed from CO dissociation [23], but X can be another chemical species altogether. This seems to provide a possibility to obtain controllable oscillations.

The Lotka model consists of just three reactions [26,27].



In the autocatalytic step A and B have to be nearest neighbors. It is infinitely fast. The remarkable thing about this model is that it shows oscillations at all. If one assumes that the behavior of the system is determined by the coverages θ_A and θ_B , then there is a theorem that states that oscillations do not occur in two-variable systems with only uni- and bimolecular reactions [28]. This means that the system is not only determined by the coverages, but one also needs correlation.

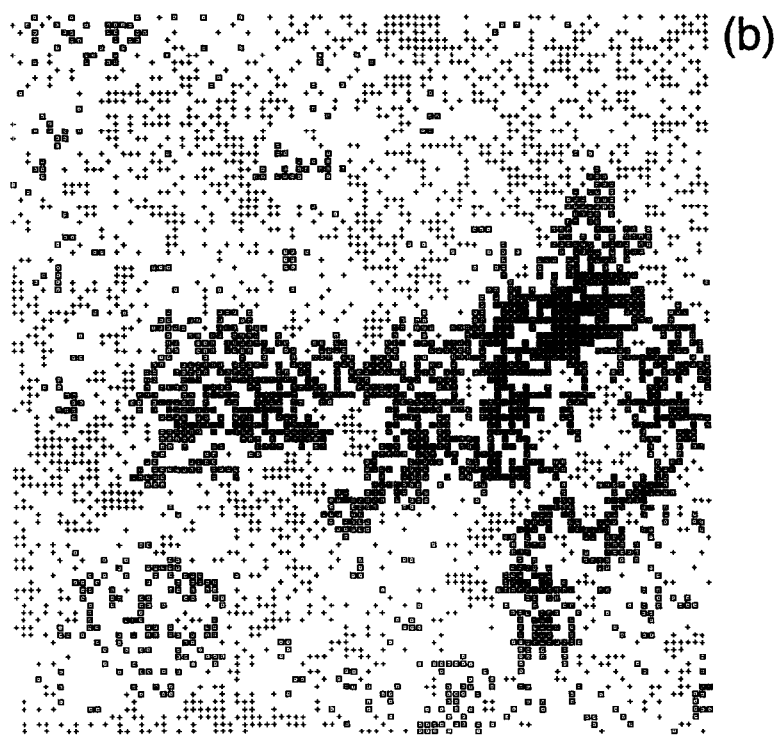
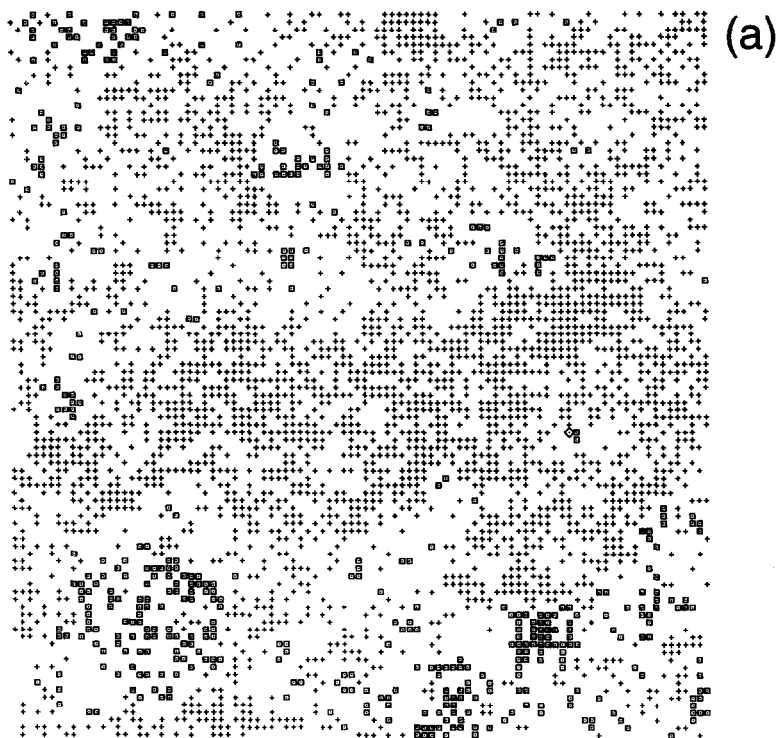
Fig. 2 shows how the coverages change in time for the two models. The unit of time for CO oxidation is chosen so that the transition probability for CO adsorption is 1. For the Lotka model the unit of time is such that the sum of the transition probabilities for A adsorp-

tion and B desorption is 1. We see that the oscillations in the Lotka model are very regular, whereas there is some variation in the amplitude and period of the oscillations in the CO oxidation. The reason for the latter is a finite-size effect. The oscillations in the CO oxidation are triggered by a fluctuation in the vacancies in the CO layer when the system is CO poisoned (see below). These fluctuations are less regular for smaller system sizes. Unfortunately, large systems, and therefore more regular oscillations, are computationally very costly.

Fig. 3 shows the trajectories of the two systems in the $(\theta_{\text{CO}}, \theta_{\text{O}})$ - and the (θ_A, θ_B) -plane, respectively. This figure hints at the mechanism in the CO oxidation that causes the oscillations. The part where the system changes very slowly (bottom-right) corresponds to the CO-poisoned state. There are very few vacancies in the CO layer, but there is quite a number of X. Consequently, X will desorb slowly, and is replaced by CO. Also at the top-left part of the trajectory the system moves slowly. This corresponds to the reactive state. In this state there are many more vacancies than there are X's. Therefore there is net X adsorption. The CO-poisoned and the reactive state are both stable when the X coverage is fixed between $\theta_X \approx 0.05$ and 0.10. With X adsorption and desorption these states evolve and become unstable, and there are transitions from one to the other. The system moves faster in the $(\theta_{\text{CO}}, \theta_{\text{O}})$ -plane during these transitions.

The more important transition is the one from the CO-poisoned to the reactive state. Below $\theta_X \approx 0.05$ the CO-poisoned state becomes unstable. When a fluctuation occurs that creates a small hole in the CO layer where oxygen can adsorb, the formation of CO_2 rapidly enlarges that hole, thus facilitating more oxygen adsorp-

Fig. 5. Snapshots of the adlayer in the Lotka model just before (a) and after (b) an avalanche of autocatalytic reactions. The A's are depicted by crosses, and the B's by squares. The avalanche is triggered by adsorption of one A at the position marked by a diamond in (a). The snapshots are obtained from a simulation with a 128×128 square grid. (Only part of the whole grid is shown.) Transition probabilities are 0.11 for A adsorption and 0.89 for B desorption. The autocatalytic reaction is infinitely fast.



tion, etc. Fig. 4a shows the adlayer during this transition. A reactive front sweeps over the whole surface. This forms the synchronization mechanism that fixes the phase of the oscillations for the whole adlayer.

Fig. 4b shows the adlayer in the reactive state. It nicely shows one function of the site blocking adsorbate. Without that adsorbate CO will not be able to form islands. However, at the lower part of Fig. 4b a CO island can be seen. It has many X's at the edge. These protect the island from being annihilated by oxygen.

The mechanism of the oscillations in the Lotka model is caused by large avalanches of the autocatalytic reaction. The system evolves towards A poisoning, as can be seen in the bottom-right part of Fig. 3b, but that state is never reached. Fig. 5 shows what typically happens. In Fig. 5a a few B's are left. Next an A adsorbs at the site marked by the diamond on the right, just below the middle. This A adsorbs next to a B and immediately is turned into a B. The same happens with the A's connected to this new B. The result is shown in Fig. 5b.

The behavior of the Lotka model is characterized by the transition probability ζ for the A adsorption. The unit of time is chosen so that the transition probability for B desorption is $1 - \zeta$. It can be shown that for the average coverages

$$\bar{\theta}_A + \frac{1}{\zeta} \bar{\theta}_B = 1 \quad (20)$$

holds. (The bar stands for time averaging.) The simulations shows that $\bar{\theta}_A < 1$ for all ζ , so that $\bar{\theta}_B \propto \zeta$ for $\zeta \rightarrow 0$. As a consequence the average size of the autocatalytic reaction avalanches is proportional to $1/\zeta$ for $\zeta \rightarrow 0$ [27]. If this size is finite we have only local oscillations, but it diverges when ζ decreases, and the oscillations become global. There is a recovery period after a large avalanche, in which no other large avalanches can occur, because few A's are left on the surface. During this recovery period there is a slow build-up of θ_A and a more rapid

decrease of θ_B due to A adsorption and B desorption.

The macroscopic rate equations for both models can be derived using the method of Section 2. For CO oxidation with site blocking one finds

$$\frac{d\theta_{CO}}{dt} = \theta_* - 0.001\theta_{CO} - 4W_{\text{reac}}\theta_{CO}\theta_O, \quad (21)$$

$$\frac{d\theta_O}{dt} = (4 \cdot 0.52)\theta_*^2 - 4W_{\text{reac}}\theta_{CO}\theta_O, \quad (22)$$

$$\frac{d\theta_X}{dt} = 0.0003\theta_* - 0.0003\theta_X, \quad (23)$$

where W_{reac} is the transition probability for the formation of CO_2 . (The other transition probabilities are as in Fig. 2.) For the Lotka model one finds

$$\frac{d\theta_A}{dt} = \zeta\theta_* - 4K\theta_A\theta_B, \quad (24)$$

$$\frac{d\theta_B}{dt} = -(1 - \zeta)\theta_B + 4K\theta_A\theta_B, \quad (25)$$

where K is the transition probability for the autocatalytic reaction. Because of $W_{\text{reac}} \rightarrow \infty$ the CO oxidation becomes trapped in the CO-poisoned state. Because of $K \rightarrow \infty$ the only stable state of the Lotka model has $\theta_A = 0$ and $\theta_B = \zeta$. The origin of these erroneous results is the implicit assumption of these rate equations that the adsorbates are randomly distributed. This and the infinitely fast step causes the coverage of one adsorbate to converge to zero. The macroscopic rate equations cannot account for the formation of well-separated islands, which allows for non-zero coverages for all adsorbates. The islands here are formed by segregation due to high reaction rates, and not to lateral interactions. For the CO oxidation it is possible to obtain oscillations with Eqs. (21)–(23), but only at the expense of changing the coefficients on the right-hand-sides. The consequence of this is that one cannot interpret these coefficients as reaction rates any longer. For the Lotka model even changing these coefficients produces no oscillations.

4. Conclusions

In this paper I have shown how the kinetics of reactions on surfaces can be modelled using a master equation that describes the evolution of a catalyst's surface and the adlayer. I have shown how to derive the equation from first principles, and how it relates to macroscopic rate equations. A Monte Carlo method to obtain numerical results has been described.

The method was used to study the oscillations in two model systems; CO oxidation with site blocking and the Lotka model. In the CO oxidation the oscillations are caused by a bistability in the CO₂ production for a range of coverages of the site blocking adsorbate. Slow adsorption and desorption of that adsorbate drive the system from one state to the other and back. The transition from the CO-poisoned state to the CO₂-producing state occurs explosively. A reaction front, moving rapidly over the whole surface during this transition, forms the synchronization mechanism. In the Lotka model the oscillations are caused by large avalanches of the autocatalytic reaction. If the ratio between A adsorption and B desorption goes to zero, the average size of the avalanches diverges, so that the oscillations become global. Neither model system can be described by macroscopic rate equations.

Finally, I would like to relate this work to studies on seemingly unrelated systems. Reactions on catalysts form just one example of phenomena that can be studied with Monte Carlo simulations of lattice–gas models. Other examples are sand piles, forest fires, and earthquakes [29], which form an active field of research in statistical physics. All these systems are formally equivalent, and I would expect that concepts that are useful to one system are also useful to others. In particular, the concepts of self-organized criticality (power-law behavior of correlations and corresponding diverging correlation lengths and times) and universality class (a limited number of sets of critical exponents; i.e., a limited number of ways for systems to

behave) might play an important role in the kinetics of catalytic processes.

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