Simulation of kinetic oscillations in surface reactions on reconstructing surfaces

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A recently introduced lattice gas model [Kuzovkov *et al.*, J. Chem. Phys. **108**, 5571 (1998)] is used for the microscopic description of surface reactions on reconstructing surfaces. The model can easily be adapted to different surface reaction systems, e.g., the $CO+O_2$, $CO+NO$, $NO+H_2$, and $NO+NH_3$ reactions. In addition many reconstructing single crystal surfaces such as Pt(100), Pt(110), Rh(100), and Rh(110) can be simulated because only those properties of the different surface phases are considered which carry the essential physics. Changes in the coordination number are neglected for the different surface phases. In the present study the CO oxidation on Pt single crystal catalysts is investigated for illustration. The model takes CO diffusion and surface reconstruction into account. Very interesting phenomena are observed besides the kinetic oscillations in the particle densities: formation of mesoscopic patterns and synchronization. Only few parameters, as there are the CO gas phase concentration y, the CO diffusion constant D, the CO desorption constant k, and the surface phase propagation velocity V are sufficient to obtain a realistic model showing regular [Pt(110)] and irregular [Pt(100)] oscillations as well as the presence and absence of spatiotemporal patterns, respectively, as observed in experiments. In addition the model gives the critical CO coverage for the surface reconstruction as a result of the model. The small number of parameters renders it possible to study the whole parameter regime and to associate the observed phenomena with these parameters. © *1999 American Institute of Physics.*
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I. INTRODUCTION

The occurrence of kinetic oscillations in catalytic surface reactions such as the oxidation of CO on Pt(100) and Pt(110) is a well-known phenomenon and has been investigated extensively in the recent past. A comprehensive overview is given in the review article by Imbihl and Ertl.[1] Experimental results show that the kinetic oscillations are closely connected with the propagation of chemical waves, i.e., with the propagation of the borders between CO and O covered regions on the catalyst surface.[1,2] In the case of the Pt(100) surface adsorbed CO is able to reverse the $1\times1\rightarrow hex$ surface reconstruction.[3–5] As O adsorbs essentially only on the 1×1 phase, which initiates the reaction, continuous structural transformations are propagated along with chemical waves. Therefore the system of the $CO+\frac{1}{2}O_2$ reaction is in principle able to show kinetic oscillations as soon as one takes these structural transformations into account. The questions that arise are, which basic processes among the vast number of proposed reaction steps have to be included to describe the kinetic oscillations and how should these elementary reaction steps be modeled on an atomic length scale.

In the case of models including the surface reconstruction computer simulations[2] and theoretical approaches[6,7] presented so far in the literature include in their treatment almost every basic reaction step proposed on the basis of experimental data (e.g., adsorption and desorption of CO and adsorption of O_2 on different surface structures, reaction via the Langmuir–Hinshelwood and the Eley–Rideal mechanism, surface structural transformation, etc.) resulting in about ten kinetic parameters. Surprisingly although many detailed steps have been taken into account, CO diffusion has so far been almost neglected in models considering the surface reconstruction, although it is a very fast and important surface process. Perhaps such an approach with many parameters is necessary and no simpler system is capable of describing the observed phenomena. But in our view it seems highly improbable that there should not be primary processes which are responsible for the structure of the oscillations and secondary ones. It would greatly improve the understanding

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of the physics if one could achieve the simplest possible model which describes correctly the observed phenomena. This should include those processes deemed *a priori* relevant in the surface reaction. Studies with such a large number of parameters as mentioned above have another disadvantage: They cannot cover the whole parameter regime but are restricted to small subsets by fixing most of the parameters on the basis of experimental data.

In the present article we give a detailed description of our model for oscillating catalytic reactions on reconstructing surfaces[8] and concentrate on the case of the $CO+O_2$ reaction on Pt(100) and Pt(110). In addition we compare our model with existing models for the oscillating CO oxidation on reconstructing Pt single crystal surfaces because there exist substantial differences between these models. Our model is the first one for catalytic reactions on reconstructing single crystal surfaces with completely local definitions of the elementary reaction processes. By a local definition is meant that all possible microscopic transitions take place on only one (monomer adsorption and desorption) or two nearest-neighbor (NN) lattice sites (dissociative dimer adsorption, diffusion, reaction, reconstruction), i.e., for all elementary processes only 1×1 or 1×2 matrices of lattice sites have to be considered. This is also the case for well-known models without oscillation phenomena such as the Ising model and the model of Ziff, Gulari, and Barshad (ZGB model) for the catalytic CO oxidation.[9] There are also models for kinetic oscillations which have been defined locally,[10–14] but these do not consider the surface reconstruction. In contrast to the local transitions occurring on one or two nearest-neighbor surface sites mentioned above we will call all three or higher point processes as defined globally because in these cases the neighborhood plays a certain role. This should not be confounded with local and global length scales.

The models which consider surface reconstruction use a somewhat mixed description of the individual processes. All chemical transitions are defined locally as in the ZGB model but the surface reconstruction is defined globally. In general a $n \times n$ matrix is used for the definition of the surface reconstruction. In the mesoscopic case[2] $n \gg 1$, in the macroscopic case[15] $n=L$ holds, where L is the lattice side length. The reason for this is the notion of a surface *phase* which can be reconstructed or nonreconstructed. This phase is necessarily a mesoscopic concept because it would be unphysical to regard a single lattice site (1×1 matrix) as a surface phase. It has been shown by experiment that adsorbate species as well as the surface phases build mesoscopic domains on a length scale ξ much larger than the lattice constant a, $\xi \gg a$.

With a local definition of the surface reconstruction one might expect surface phase fluctuations on the length scale of $\xi \sim a$. This would be completely unphysical. On the other hand a global definition of the reconstruction leads only to a fictitious solution of the problem. In the Monte Carlo (MC) investigations of the surface reconstruction generally $n=3$ and $n=L$ have been used.[2,15] In the first case $\xi=3a$ does not really correspond to a mesoscopic length scale; in the second case all basic and interesting processes such as nucleation and the growth and decline via phase border propagation of the individual surface phases are wiped out. Therefore the

global definition of the surface reconstruction only results in additional difficulties for the simulation procedure. Even worse is the fact that these models cannot be treated with the known analytical methods[16] (mean-field approximation, pair mean-field approximation,[17] cluster approximation,[18] and correlation analysis)[19] because these are developed for models defined locally.

From the theory of critical phenomena and phase transitions[20,21] it is known that a so-called correlation length $\xi \gg a$ can develop in systems with only short range interactions of the order of a. Let us consider the well known Ising model with two microscopic states α (spin up) and β (spin down). At sufficiently high temperatures $T \gg T_0$ with T_0 the critical temperature the α and β states are equally probable and randomly distributed, i.e., the individual α and β domains build islands of length $\xi \sim a$. With decreasing temperature in the temperature range of the paramagnetic phase $T \sim T_0$ the α and β states are arranged in mesoscopic islands whose length $\xi \gg a$ diverges for $T \rightarrow T_0$. Within the ferromagnetic phase $T < T_0$ a macroscopic matrix of a single phase, e.g., the α phase, is formed because of spontaneous symmetry breaking. In this macroscopic α domain there exist finite, mesoscopic islands of the β phase. Therefore it is possible to get real mesoscopic domains with $\xi \gg a$ resulting from purely microscopic (local) definitions in a certain parameter regime (here $T \sim T_0$). Of course small fluctuations exist on the length scale of a. Although these are damped and occur only very rarely, their existence is important in order to understand the processes of nucleation and growth of microscopic nuclei into mesoscopic domains.

Here we will define the surface phase in a similar way, i.e., the individual lattice sites are given a certain ''spin'' variable χ, with $\chi \in [\alpha, \beta]$. In our model α and β denote the reconstructed and nonreconstructed surface phase, respectively. These two states of the lattice sites can be changed *locally* via certain rules given below. Whether these local rules will lead to mesoscopic phase distributions depends on the kinetic parameters (i.e., the definition) of the model.

First we briefly discuss the two processes of the nucleation and the growth and decline of surface phases used in previous models. It is known from experiment that the surface reconstruction takes place if the coverage of certain adsorbates (e.g., CO or NO) increases above or drops below a certain critical value. In the first case the reconstruction is lifted, whereas in the second case the surface reconstructs. In the $CO+O_2$/Pt(100) system considered here a value of $\Theta_{CO,crit} \approx 0.3$ of this critical coverage has been measured experimentally.[4] For $CO+O_2$/Pt(110) it has been determined to $\Theta_{CO,crit} \approx 0.2$.[1] Note that these values are only approximately known. In mathematical models based on the mean-field (MF) approximation this critical concentration is used as a parameter taken from experiment. In a similar way it is used in models based on lattice gas simulations. The problem in the case of simulations is the arbitrary choice of the values for the critical CO coverage which vary between 0 and 1, as shown in the following.

In a paper by Albano[15] the macroscopic global definition of the surface reconstruction is used. In this model for the

$CO+O_2/Pt(100)$ system the surface reconstructs if the global (fractional) CO coverage Θ_{CO} on the lattice drops below 0.1. In this case *all* $N=L^2$ lattice sites are switched from the β state into the α state. Because O_2 cannot adsorb onto this α phase the CO coverage increases. If the CO coverage reaches $\Theta_{CO}=0.485$ all N lattice sites are changed back into the β state because the surface reconstruction is lifted by CO. Now O_2 can adsorb and CO is removed from the surface via $CO+O$ reaction and the cycle starts over again. It is obvious that this mechanism has to lead to global and regular oscillations in the CO_2 reaction rate. However, only irregular oscillations have been generally observed in the $CO+O_2/Pt(100)$ system, but these cannot be described with the global definition of the surface reconstruction. Regular oscillations on Pt(100) have been observed but are rather the exception and usually stable only over a small number of periods.[7,22] Another weakness is the somewhat arbitrary choice of the critical values for the CO coverage where the reconstructions take place. As stated above the investigation of nucleation and growth processes is impossible in the framework of a macroscopic global definition of the reconstruction process. Surface diffusion of CO is neglected in this study.

In an article by Möller *et al.*[2] the mesoscopic global definition of the surface reconstruction is used with $n=3$. The lifting of the reconstruction ($hex \rightarrow 1\times1$) occurs on a central hex site if eight sites of the eight neighbors (Moore neighborhood) and the central site itself are covered by CO. This corresponds to a critical CO coverage of $\Theta_{CO} \approx 0.9$ on the mesoscopic length scale and the approach is justified via local fluctuations. For the $1\times1 \rightarrow hex$ transition $n=1$ is used. Thus an empty 1×1 site can transform into an empty hex site, even if all adjacent sites are covered by CO. This corresponds to a local critical CO coverage of $\Theta_{CO}=0$. The surface reconstruction in Ref. 2 is based exclusively on nucleation processes because the phase of neighbor sites plays no role. The surface phase transition depends only on the coverage of the central and the adjacent sites. A growth process depending on the phase of neighboring sites is not considered. Surface diffusion of CO is mentioned but has only a weak influence on the system behavior by increasing the velocity of wave propagation without altering the qualitative picture.

Very recently Gelten *et al.*[23] have introduced a model which uses globally defined mesoscopic nucleation and a locally defined growth process. In addition the model includes a geometric transition between the surface phases, where the 1×1 phase is modeled by the square lattice with the coordination number $z=4$ and the hex phase by the hexagonal lattice with $z=3$. The nucleation of the 1×1 phase takes place if five nearest-neighbor (NN) hex sites are covered by CO ($n=3$). In this case the central three NN hex sites are transformed into 1×1 sites. For the hex nucleation one empty 1×1 lattice site is considered sufficient. In addition to these nucleation processes the border of already formed phase islands can propagate as follows. If a CO is adsorbed on a hex site next to a 1×1 island, this site can be transformed into the 1×1 phase (island growth by trapping). In this case the growth process is directly combined with the adsorption of CO. In this model surface diffusion of CO is

addressed only very shortly and leads to the synchronization of the oscillations. In both models in Refs. 2 and 23 the nucleation occurs depending on the presence or absence of CO.

In Sec. II we give a detailed description of our model for oscillating surface reactions on reconstructing surfaces in which we direct our special attention to the local definition of the individual reaction steps. In addition different starting points for the extension to other surface reaction systems are briefly presented. In Sec. III the results such as the existence of irregular oscillations on Pt(100) and regular oscillations on Pt(110) as well as the CO diffusion as a mechanism of synchronization are presented. Conclusions are drawn in Sec. IV.

II. THE MODEL

A. General aspects

In our study we want to abstract from many details of the real surface reaction system and consider only a very simplified model for kinetic oscillations in the catalytic CO oxidation on Pt(100) comparable to the well known ZGB model[9] for the $CO+\frac{1}{2}O_2$ surface reaction. To emphasize these simplifications we will deal with a model for the $A+\frac{1}{2}B_2 \rightarrow 0$ reaction where A and B stand for CO and O, respectively. The product AB (CO_2) spontaneously desorbs from the lattice resulting in the annihilation of an AB pair and leaving two vacant nearest-neighbor sites. Furthermore we consider the structural transformation $\alpha \rightleftharpoons \beta$ on the square lattice with coordination number $z=4$ and the lattice constant a, where α and β stand for the hex [1×2] and 1×1 phase on real Pt(100) [Pt(110)] catalysts. In our model only the different physical but not geometrical properties of the phases are considered because it is impossible to give a *local* geometric specification of the phase. The occupation of the lattice is denoted by X with $X \in \{0,A,B\}$ which stands for an empty site, a site occupied by A, or by B, respectively. In addition the site itself belongs to the phase χ with $\chi \in \{\alpha,\beta\}$. For example, A^β stands for a lattice site of phase β which is covered by A. The model uses the principal rules of the ZGB model. We will show that this renders it possible to use a reaction model with only few parameters and the following characteristical properties:

(a) All parameters have a clear physical meaning. They define (i) the composition of the gas phase, (ii) the diffusion and desorption of the mobile surface species and (iii) the propagation of the 1×1 and hex reconstructed surface structure. This small number of parameters makes it possible to comprehensively investigate the model and to associate the phenomena occurring with these parameters. All aspects of this system show an unambiguous dependence on these parameters.

(b) The oscillations in the catalytic CO oxidation on both the Pt(100) and the Pt(110) surface can be simulated by the same model using only slightly different parameter sets because the basic mechanisms are identical on both surfaces.[1]

(c) The kinetic parameter of the oscillations has the same order of magnitude as the other parameters with the exception of the very fast diffusion. This makes it easy to apply Monte Carlo simulations. In addition we have developed a very fast cellular automaton approach to simulate the reaction on large lattices.[24]

(d) All basic reaction steps correspond to monomolecular or bimolecular steps, respectively. Processes on a mesoscopic length scale are not used. The simple structure of the reaction equations permits the use of different analytical approximation tools such as the MF approximation, the cluster approximation,[18] or the correlation analysis.[19] These approaches will be considered in a separate paper.[25]

(e) A simplified analytical analysis shows that the critical CO coverage $\Theta_{CO,crit} \approx 0.3$ for the surface reconstruction can be obtained as a *result* from our model, it is not an input.

B. Transition rates

A kinetic model of the Markovian type is completely defined via its state variables σ and the possible transitions which can occur. In our present model we only consider monomolecular and bimolecular steps and therefore get very simple kinetic definitions of the individual transitions. Monomolecular steps are the simplest processes because only one state variable $\sigma_l = X^\chi$ changes:

$$\sigma_l \overset{p}{\Rightarrow} \sigma_l', \quad \text{with} \quad p \equiv P(\sigma_l \rightarrow \sigma_l'). \tag{1}$$

σ_l is the state of lattice site $\vec{l}$. p is the transition rate for this process which is independent of the neighborhood.

Bimolecular steps describe processes which change two state variables σ_l, σ_m. In our model only processes which change the states of two nearest neighbor sites with $|\vec{l} - \vec{m}| = 1$ are considered:

$$\sigma_l \sigma_m \overset{q}{\Rightarrow} \sigma_l' \sigma_m', \quad \text{with} \quad q \equiv \frac{1}{z} Q(\sigma_l \sigma_m \rightarrow \sigma_l' \sigma_m'). \tag{2}$$

Here q is the corresponding transition rate. Again, the transition rates for these bimolecular processes only depend on the states of the two nearest-neighbor sites.

C. Nucleation

In our model both the nucleation and the growth process are defined locally. Furthermore all parameters correspond to elementary processes with a clear physical meaning and no parameter has to be taken from experiment. It is just the opposite to the normal situation; we can show that the critical CO concentration emerges from our model. We assume that both the α and the β phase of the Pt surface are stable or metastable in the course of the reaction, where metastable means that a homogeneous phase can stay homogeneous for a long time. Therefore nucleation is considered as a very rare process which corresponds to very small kinetic transition rates. In this way the mesoscopic homogeneity can be explained. The simplest way to introduce nucleation into the

model is to consider nucleation as a local transition of the phase of one individual site. This transition is independent of the neighborhood and the coverage of the site, i.e., it does not depend on the presence or absence of CO. Therefore it can be seen as a weak noise which creates small defects in an otherwise homogeneous phase and corresponds to a local $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ transition, respectively. We suppose that both processes have the same transition rate γ:

$$P(X^\alpha \rightarrow X^\beta) = P(X^\beta \rightarrow X^\alpha) = \gamma, \quad \text{with} \quad X \in \{0, A, B\}. \tag{3}$$

These defects will be annihilated or will start to grow to mesoscopic phases depending on certain conditions (adsorbate coverages, kinetic transition rates, etc.). The fact that the nucleation is modeled as a very rare process allows one to neglect this process in a first approximation. In this case we assume that the heterogeneous state has already been created by the nucleation process and investigate the development of this heterogeneous state as a consequence of the growth process. One important result of our model is that the heterogeneous state remains heterogeneous in a certain parameter regime. The system shows a dynamically stable heterogeneity in form of oscillations even without nucleation. This allows us to use randomly distributed surface phases as an initial condition and to neglect the nucleation process which has been introduced here only for the reason of completeness of the model. The nucleation process is not considered in the present study and will be the aim of our future work.[26]

D. Phase propagation

Although the interior domains of the surface phase islands are stable (we neglect nucleation) there exists an instability in the system which comes from the phase border of the individual phase islands. If one considers growth processes the physical system will try to reach homogeneity and remove the gradients of the phase concentrations. We assume that only the growth process of the surface phase border depends locally on the presence or absence of CO. This is in agreement with the results of island growth rate measurements by King and co-workers,[27] which are very often misinterpreted as nucleation rates. Consider a pair of NN sites where the individual sites belong to different surface phases, i.e., the state of the pair of NN sites is $\alpha\beta$. If at least one of these two sites is covered by CO the phase border propagation $\alpha\beta \rightarrow \beta\beta$ is induced. If CO is absent on these two sites the inverse phase transition $\alpha\beta \rightarrow \alpha\alpha$ occurs.

$$Q(A^\alpha X^\beta \rightarrow A^\beta X^\beta) = V \quad \text{with} \quad X \in \{0, A, B\}, \tag{4}$$

$$Q(A^\beta X^\alpha \rightarrow A^\beta X^\beta) = V \quad \text{with} \quad X \in \{0, A, B\}, \tag{5}$$

$$Q(X^\alpha Y^\beta \rightarrow X^\alpha Y^\alpha) = V \quad \text{with} \quad X, Y \in \{0, B\}. \tag{6}$$

The presence or absence of CO is important only directly at the border between the different surface phases, contrary to the global definition of the reconstruction via a global critical CO coverage. The availability of CO at the phase border determines which phase (α or β) grows and which one declines. Because the number of CO molecules at the border is small, CO diffusion supports the phase border propagation. Because CO diffusion is the most prominent process in the

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catalytic CO oxidation, the $\alpha\beta\to\beta\beta$ phase border propagation can occur even at relatively low global CO coverages.

E. *A* adsorption and desorption

The adsorption of a particle A from the gas phase is modeled as in the ZGB model and the probability for A adsorption is given by the gas phase concentration $y=y_A$:

$$P(0\to A)=y. \tag{7}$$

The desorption of a particle A from the surface is modeled in a similar way with desorption rate k:

$$P(A\to 0)=k. \tag{8}$$

F. B_2 adsorption

A B_2 particle is adsorbed with probability $2s_\chi(1-y)$ if two empty nearest-neighbor sites are found.

$$Q(00\to BB)=2s_\chi(1-y). \tag{9}$$

Here $y_B=1-y$ is the gas phase concentration of B_2 and s_χ is the B_2 sticking coefficient on phase χ with $s_\beta=1$ and $0\le s_\alpha\le 1$. For Pt(100), $s_\alpha=0$ and $s_\beta=1$ are chosen, whereas $s_\alpha=0.5$ and $s_\beta=1$ are used for Pt(110) as the default values. These values are in qualitative agreement with experimental data.[1] Note that this difference in the values of the sticking coefficients $s_\alpha=0$ and $s_\alpha=0.5$ is the only difference in modeling the Pt(100) and Pt(110) surface, respectively. For a detailed study of the influence of the sticking coefficients see Ref. 8.

G. *A* diffusion

In our model the surface diffusion of A is defined via the transition rate

$$Q(A0\to 0A)=D. \tag{10}$$

The diffusion is modeled as a jump of an A particle onto an empty nearest-neighbor site. It can be shown that for the diffusion coefficient of A diffusion on an otherwise empty lattice the equation $D_A=(1/z)a^2D$ holds, where a is the lattice constant and z the coordination number of the lattice. Therefore our parameter D corresponds to the frequency factor for the diffusion (all transition rates in the stochastic theory are of dimension $[t]^{-1}$).

The diffusion of CO plays two roles in our model. On the one hand CO diffusion in combination with the surface phase propagation leads to the existence of the critical CO coverage for the surface reconstruction (see below). On the other hand CO diffusion causes local synchronization of the kinetic oscillations. Therefore large values of the diffusion rate are an attribute of our model. Although it is known that diffusion is one of the fastest and most prominent elementary processes on surfaces it is almost neglected in microscopic models for oscillating surface reactions so far, with only few exceptions where only slow diffusion has been considered, however (see above).

H. *AB* reaction

In contrast to the ZGB model we define the reaction rate of the AB reaction via
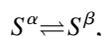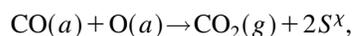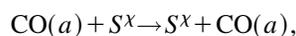
$$Q(AB\to 00)=R, \tag{11}$$

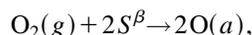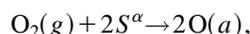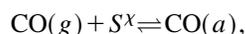with finite R. In the original ZGB model this parameter is removed because the limit of an infinite reaction rate $R\to\infty$ is used; but using this limit cannot be described with only monomolecular and bimolecular reaction steps. For example, the B_2 adsorption with an A particle on a nearest-neighbor site would lead to the chain process

$$00A\to[BBA]\to B00, \tag{12}$$

which corresponds to a trimolecular process. To avoid dealing with such higher order processes we remove the reaction parameter in a different way by simply setting R sufficiently large. In a previous study we have shown that saturation occurs if R exceeds a certain value R'.[24] For $R>R'$ the system behavior corresponds to a system with infinite reaction rate. For simulations with fast surface diffusion the parameter can be removed by changing the reaction mechanism. In this case reaction occurs when an A particle hops to a NN site which is occupied by B, and $R=D$ holds.[24]

I. Kinetic schemes

Summarizing the above transition definitions we simulate the following model written in the more usual form of reaction equations. For the CO+O$_2$ reaction we use

$$CO(g)+S^\chi\rightleftharpoons CO(a),$$

$$O_2(g)+2S^\alpha\to 2O(a),$$

$$O_2(g)+2S^\beta\to 2O(a),$$

$$CO(a)+S^\chi\to S^\chi+CO(a),$$

$$CO(a)+O(a)\to CO_2(g)+2S^\chi,$$

$$S^\alpha\rightleftharpoons S^\beta,$$

where S stands for a free adsorption site, χ stands for either α or β and (a) or (g) for a particle adsorbed on the surface or in the gas phase, respectively. Note that in the model simulated here O$_2$ adsorbs onto sites belonging to the α or β phase with different sticking coefficients. For additional details see Ref. 8

The model is simulated by means of a cellular automaton (CA) technique[24] on square lattices with side lengths varying from $L=128$ up to $L=4096$ using periodic boundary conditions. In this approach pairs of NN sites are chosen in parallel instead of sequentially in a random order as it is done in Monte Carlo simulations. Because we only consider pairs of NN sites a graphical representation of the CA rules

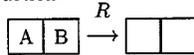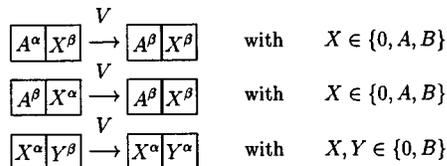corresponding to the reaction equations above can be shown.

Adsorption:

$$\square\,\square \xrightarrow{y} \boxed{A}\,\square \qquad\qquad \square\,\square \xrightarrow{2s_\chi(1-y)} \boxed{B}\,\boxed{B}$$

Diffusion and Desorption:

$$\boxed{A}\,\square \xrightarrow{D} \square\,\boxed{A} \qquad\qquad \boxed{A}\,\square \xrightarrow{k} \square\,\square$$

Reaction:

$$\boxed{A}\,\boxed{B} \xrightarrow{R} \square\,\square$$

Reconstruction:

$$\boxed{A^\alpha}\boxed{X^\beta} \xrightarrow{V} \boxed{A^\beta}\boxed{X^\beta} \qquad \text{with} \qquad X \in \{0, A, B\}$$

$$\boxed{A^\beta}\boxed{X^\alpha} \xrightarrow{V} \boxed{A^\beta}\boxed{X^\beta} \qquad \text{with} \qquad X \in \{0, A, B\}$$

$$\boxed{X^\alpha}\boxed{Y^\beta} \xrightarrow{V} \boxed{X^\alpha}\boxed{Y^\alpha} \qquad \text{with} \qquad X, Y \in \{0, B\}$$

This model definition allows us to change or add new reaction steps or transition rates very easily. Also the geometry can be changed to the triangular lattice in order to simulate surfaces with coordination number $z = 6$ because only the physical properties of the individual phases are considered. The model has been adapted to the CO+NO reaction[28] on Pt(100) where the two surface phases show different dissociation rates for NO.

III. RESULTS AND DISCUSSION

One of the most important properties of our model is the existence of a critical CO coverage $\Theta_{CO,crit}$ as an inherent result of the model itself. It is the first model which does not use some sort of critical coverage in order to induce the surface reconstruction. Consider randomly distributed surface phases α and β each with an initial concentration of $\Theta_\alpha = \Theta_\beta = 0.5$. The surface is covered with A exclusively and further adsorption or reaction processes are not considered. Therefore the coverage of A remains constant and the relaxation process of the surface phases can be investigated as a function of the A coverage Θ_A. Only the transition rates for A diffusion, D, and the surface phase propagation V have to be considered as parameters for this simplified relaxation model. Figure 1 gives the temporal evolution of the coverage Θ_β of the β phase for different values of the A coverage Θ_A. As can be clearly seen in Fig. 1 there exist two critical values of Θ_A. For $\Theta_A < \Theta_A^{(1)}$ only the homogeneous α phase is stable, i.e., the small initial α islands grow very quickly until they cover the whole lattice because the coverage Θ_A is too small to induce the $\alpha \to \beta$ phase transition which corresponds to the lifting of the reconstruction on real Pt surfaces. For values $\Theta_A > \Theta_A^{(2)}$ only the β phase is stable because the surface concentration of A is too large for the $\beta \to \alpha$ transition to occur. This is equivalent to the complete lifting of the surface reconstruction at high CO surface coverages on real Pt surfaces. The heterogeneous distribution of the α and β phases remains heterogeneous in a dynamically stable state only for values of Θ_A between these two critical coverages of A with $\Theta_A^{(1)} < \Theta_A < \Theta_A^{(2)}$. As shown in Fig. 1 the values of
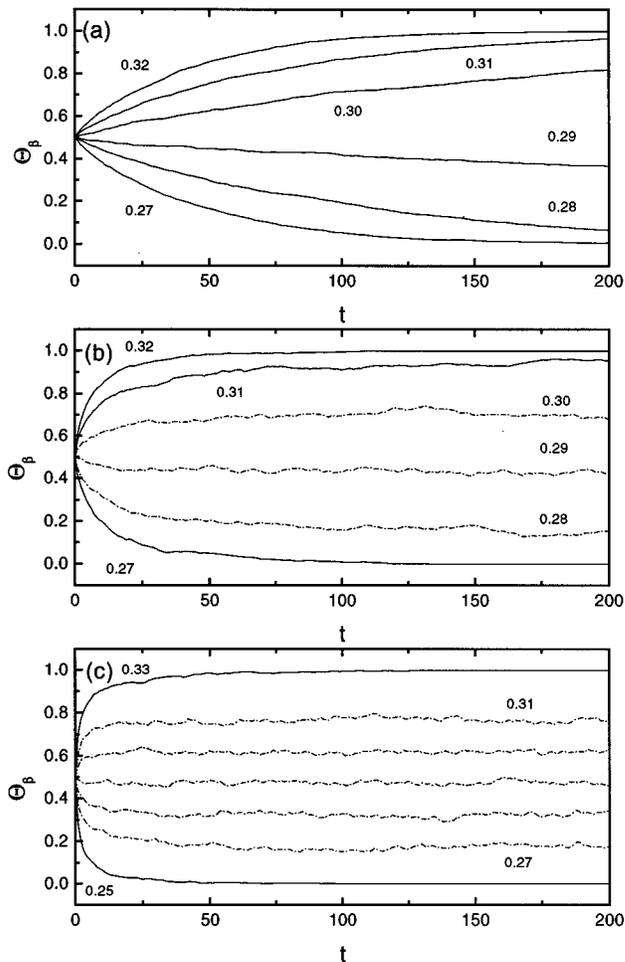

FIG. 1. MC simulation of the reconstruction with $D = 100$ and $V = 1$ (a), $V = 10$ (b), and $V = 20$ (c). The temporal change of the β coverage Θ_β is shown for different values of the A coverage Θ_A given by the numbers at the lines. The solid lines correspond to the domain of the stable homogeneous α or β phase, the dot-dashed lines show the domain of the heterogeneously stable state.

$\Theta_A^{(1)}$ and $\Theta_A^{(2)}$ depend on the parameters V and D. We will show in a separate paper[25] that the MF approximation fails to correctly describe almost every property of the system with only one exception: the critical values of Θ_A. Here we only give the result of the analysis of the critical properties of the simplified relaxation model in Ref. 25. The critical coverages depend on the ratio V/D of the phase propagation velocity V and the diffusion constant D:

$$\Theta_A^{(1)} = \frac{1}{2 + V/D + \sqrt{(1 + V/D)^2 + 1}}, \tag{13}$$

$$\Theta_A^{(2)} = \frac{1 + V/D}{2 + V/D + \sqrt{(1 + V/D)^2 + 1}}. \tag{14}$$

In the physically significant case of $D \gg V$ these two critical values coincide at

$$\Theta_A^{(1)} \approx \Theta_A^{(2)} \approx 1 - \frac{1}{\sqrt{2}} \approx 0.293, \tag{15}$$

which agrees qualitatively with the experimentally determined values of 0.3 and 0.2 for Pt(100) and Pt(110), respectively.[1,4] The value of $\Theta_{A,\text{crit}} = 0.293$ is the upper limit for $\Theta_A^{(1)}$ and the lower limit for $\Theta_A^{(2)}$. This can be seen in Fig. 1(a) where the ratio V/D is so small that $\Theta_A^{(2)} - \Theta_A^{(1)} < 0.01$ holds and no heterogeneous state has been achieved in the simulations. In Figs. 1(b) and 1(c) this stable heterogeneous solution exists. An additional result is the linear dependence of the β phase coverage Θ_β on the A coverage Θ_A, which is deduced from the equal distances between the lines for different parameter values of Θ_A. This result can also be determined from the MF approximation as a third and heterogeneous solution

$$\Theta_\beta = \frac{\Theta_A - \Theta_A^{(1)}}{\Theta_A^{(2)} - \Theta_A^{(1)}}, \tag{16}$$

in the interval $\Theta_A \in [\Theta_A^{(1)}, \Theta_A^{(2)}]$, i.e., the surface phase coverage strongly depends on Θ_A in this interval.[25] In this context it has to be mentioned that these critical values correspond to a model system without any chemical processes such as adsorption and reaction. In our model for oscillating surface reactions with the adsorption of A and B_2 and the resulting $A + B$ reaction, the critical values remain indeterminate. The advantage of our model is that we do not have to care about the values of the critical coverages because they are only hidden but always present. Another important property of our model consists in the dynamic stability of a heterogeneous state. In a certain range of the parameters y, D, k, and V a heterogeneous state of the lattice remains in this state, although no steady state exists and oscillations occur in the coverages, the reaction products, and the α and β phases of the lattice. These states are characterized by the particular type of spatial structures of lattice phases and surface particle distributions which are analyzed with snapshots of the lattice (see below, Fig. 6). Because of the temporal self-organization and the relaxation into particular heterogeneous spatial structures we only took very simple initial conditions into account: The lattice is initially empty and the sites belonging to the α and β phase are chosen at random with equal probabilities. These initial conditions have a certain drawback because the distribution of the clusters of the phases is nearly microscopic but seldom mesoscopic in size. Therefore the lattice phases exhibit a large amount of short-range structural fluctuations at the very beginning of the simulation. As a consequence the range of the parameter values, for which dynamical stability is obtained, is smaller compared to other initial conditions with mesoscopic phase distributions and without these short-range fluctuations. The differences are about 10%. Therefore we do not discuss other initial conditions and determine the critical values (e.g., for y) with an accuracy of only two digits.

The main result is the dynamical stability where the system remains heterogeneous for parameters in a finite range. For these parameters all macroscopic variables such as lattice coverages, reaction rates, and the phase concentrations show irregular oscillations for Pt(100) and regular oscillations for Pt(110) (see Figs. 2 and 3, respectively). The power spectrum clearly shows the existence of one basic frequency ω_0

which depends on the individual parameters $\omega_0 = \omega_0(k, V, D, y)$. At constant y the basic frequency increases with increasing k and V and decreases with D as $\omega_0 \sim k\sqrt{V/D}$. The distribution of frequencies around ω_0 which can be seen in the power spectrum depends mainly on the synchronization conditions determined by the above parameters. Clearly, for finite lattices, L is an additional parameter.

The oscillating solution exists in a range of $0 < y < y_c$ with the critical gas phase concentration $y_c = y_c(D, V, k)$. With increasing D and constant V, y_c decreases. For example y_c has the values $y_c \approx 0.35$ at $D = 100$ and $y_c \approx 0.20$ at $D = 1000$ for $V = 1$ and $k = 0$ on Pt(100). For values $y > y_c$ only a stationary and homogeneous solution with $\Theta_\beta = 1$, i.e., only the β phase exists. The system now corresponds to the ZGB model with diffusion except for the finite reaction rate. Because at the transition $\Theta_\beta \to 1$ almost 90% of the lattice is covered with A in many cases where $y > y_c$ and in all cases where $y \gg y_c$ the system goes into an absorbing state $\Theta_A = 1$, where the lattice is completely covered with A if A desorption is neglected. The consideration of A desorption removes the existence of this absorbing state. For $y < y_c$ oscillations exist, whereas for $y > y_c$ the system reaches a homogeneous β phase and now corresponds to the ZGB model with A desorption, i.e., it shows a reactive steady state without any oscillations. The value of y_c increases with increasing A desorption, e.g., $y_c > 0.55$ holds for $k = 0.1$.

Experiments on the CO oxidation on Pt(100) show irregular oscillations in the reaction rate in the form of wave trains[7,22] integrated over 20–50 mm^2, whereas regular and synchronized oscillations are generally found on Pt(110). In addition, no regular patterns or oscillations on the μm scale have been observed on Pt(100) in the domains between the traveling reaction fronts,[22,29] whereas on Pt(110) a rich variety of spatiotemporal patterns has been found.[1] Because we get similar results in our very simple model we have to show that nontrivial reasons are responsible for it. At first we investigate the relation between the power spectrum and the lattice side length L. In Fig. 4 one can see clearly that the basic frequency ω_0 remains constant independent of L, but the amplitudes of the oscillations show a strong dependence on L. On a lattice with $L = 128$ the system shows fluctuations with large amplitudes in all macroscopic variables. On larger lattices the amplitudes decrease with L with a remarkable drop between $L = 256$ and $L = 512$. On a lattice with $L = 4096$ the amplitudes are very small and the oscillations are almost removed [note that this lattice size models a surface area of only 1 μm^2 on Pt(100)]. Therefore the question about the synchronization of the oscillations arises. In our model the oscillations are local and exist only in a certain and finite domain on the lattice which can be characterized by its length l. If we choose the parameter $L < l$ synchronization is possible and we get oscillations with large amplitudes. If $L \gg l$ holds (large lattices) there are a vast number of local oscillations in small domains. These local oscillations are not synchronized resulting in the cancellation of oscillations on length scales of about 1 μm in the macroscopic observable variables such as the reaction rate or the surface phases. The basic reason for this is the absence of regular spatiotemporal patterns. This phenomenon has also been observed in experi-
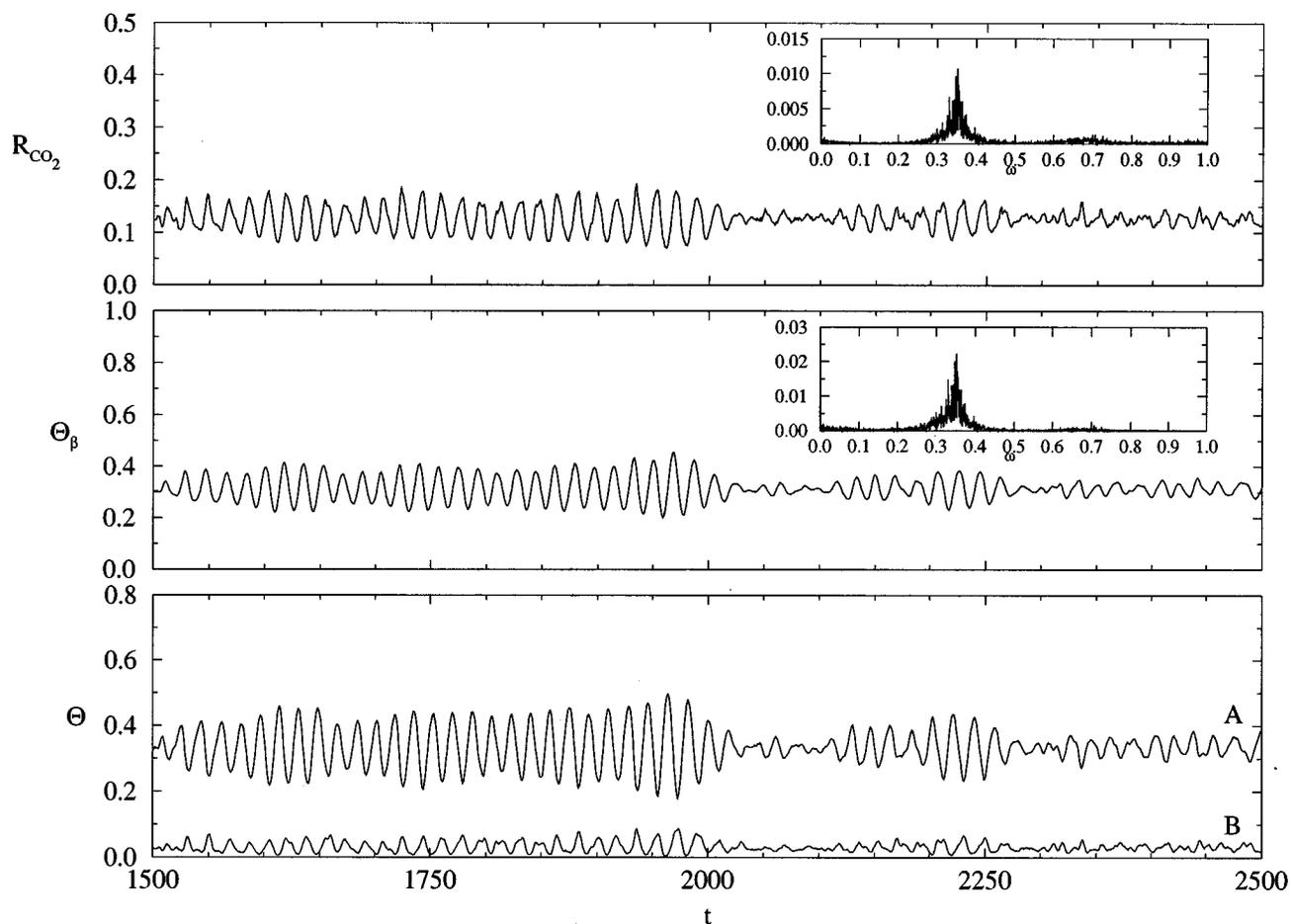
FIG. 2. Irregular oscillations in all macroscopic variables on Pt(100): the reaction rate R_{CO_2}, the fractional surface coverage Θ_β of phase β, and the fractional adsorbate coverages Θ_X with $X \in \{A, B\}$ for the parameter set $y = 0.2$, $D = 100$, $V = 1$, and $L = 256$. The insert gives the power spectrum.

mental studies.[1] In the simulations these independently oscillating domains can directly be seen. For the local oscillations V determines the basic frequency, but the growth and decline of each phase domain is a stochastic process. Thus the frequencies of these local oscillations are slightly different. This leads to beats and the frequency distributions shown in Fig. 2. On Pt(110) the synchronization is much more effective as can be seen in Fig. 3, where regular oscillations on Pt(110) in all variables are shown. But also these are only locally synchronized, because regular oscillations do not exist on larger lattices with $L > 2000$. However, in comparison with macroscopic oscillations occurring on real Pt(110) surfaces which would have to be represented by lattices of side length $L \sim 10^5 - 10^6$ there have to be other mechanisms of synchronization in addition to the surface diffusion which are currently not included in our model.

In the model considered here the diffusion of A is the mechanism of the synchronization. This can be seen in Fig. 5 where simulations with D up to $D = 1000$ are shown. The results exhibit completely new phenomena in the power spectrum. With $D = 0$ only small and very local oscillations exist, which are of the same order of magnitude as the stochastic noise and therefore cannot be seen in the power spectrum but only in the simulation. As discussed above, with

$D = 100$ there is a certain frequency distribution around one basic frequency ω_0. With $D = 1000$ one finds in the power spectrum some properties of a limit cycle (i.e., a series of frequencies $\omega_0, 2\omega_0, 3\omega_0, \dots$). The small satellite peaks show that the oscillations have not yet reached the limit cycle, but from the observed tendencies one can expect that for large D and small L global synchronization should be possible resulting in regular oscillations but only on a small lattice. The synchronization length depends on D, $l = l(D)$. Within these domains synchronized oscillations occur. Due to the finiteness of l (for finite D) it is in principle impossible to get macroscopic regular oscillations. Note, however, that the diffusion on Pt(110) is much more effective because of the formation of macroscopic surface phase domains (see below).

The question about the influence of the diffusion is a very important one because diffusion is a very fast process in the system. Most theoretical investigations used a coupling between the surface and the gas phase (sometimes a direct coupling neglecting the adsorption process) to explain the synchronization of oscillations in spatially separated domains on the surface and neglect the diffusion of adsorbate particles. In our model diffusion is the coupling process for locally synchronized oscillations in the μm range. Because
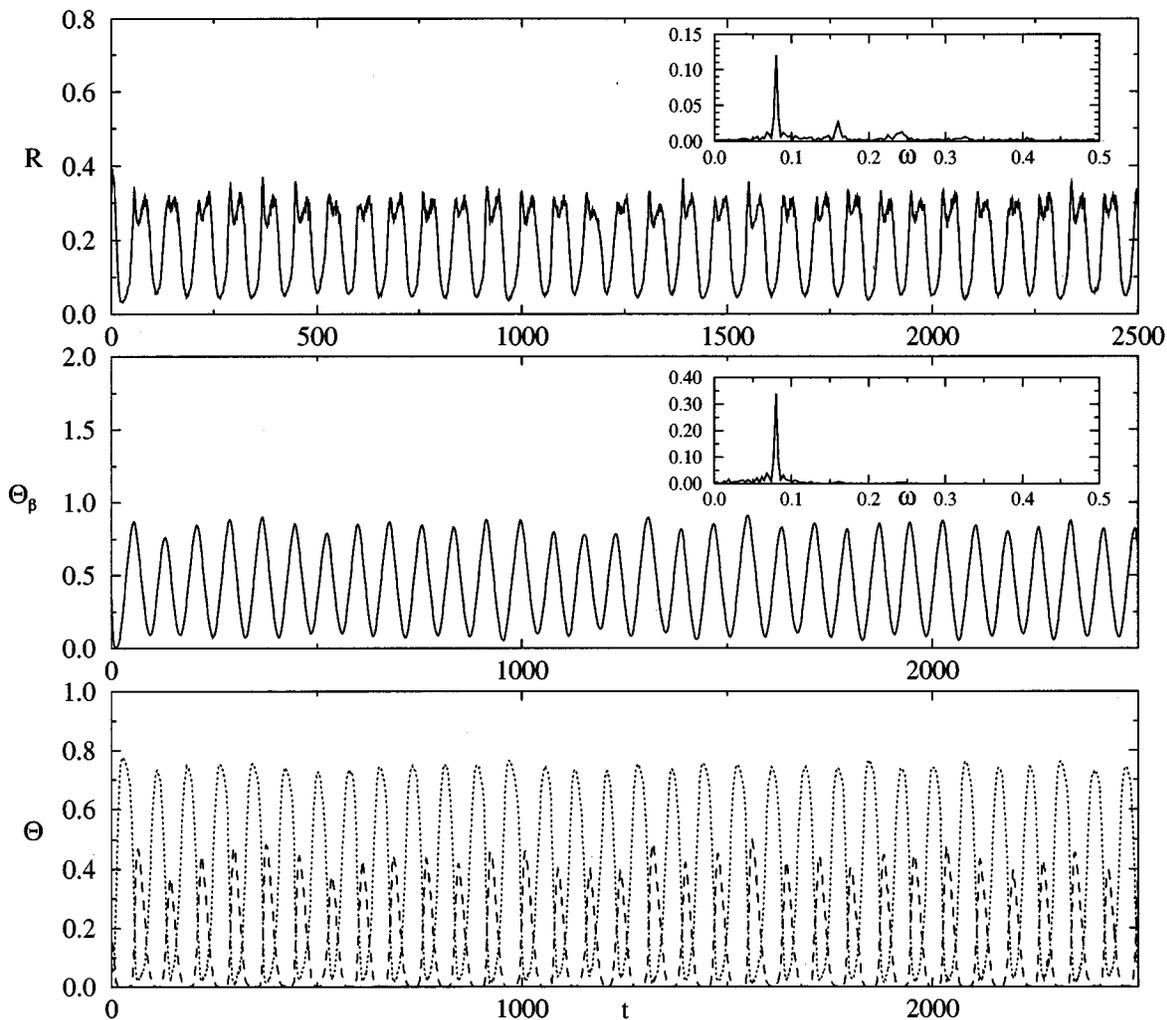
FIG. 3. Regular oscillations in all macroscopic variables on Pt(110): the reaction rate R_{CO_2}, the fractional surface coverage Θ_β of phase β, and the fractional adsorbate coverages Θ_X with $X \in \{A,B\}$ for the parameter set $y = 0.49$, $D = 100$, $V = 1$, $k = 0.1$, and $L = 256$. The insert gives the power spectrum.

surface diffusion is strongly dependent on the temperature $D = D(T) \propto \exp(-E_{diff}/k_B T)$ it is possible to examine the influence of the temperature and thus decide on the role of diffusion.

The weak synchronization of the oscillations on Pt(100) can be explained by a special structural property of the model. In the parameter range where oscillations occur the coverage by one of the surface phases (i.e., the α or β phase)
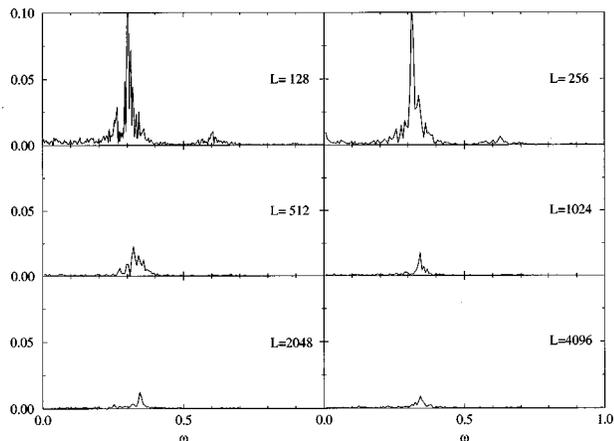

FIG. 4. Power spectra of the oscillations in the reaction rate on Pt(100) for $y = 0.2$, $D = 100$, and $V = 1$ for different lattice side lengths L.
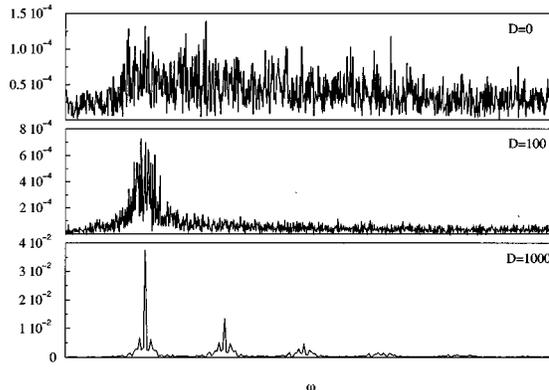

FIG. 5. Power spectra for Pt(100) with $y = 0.1$, $V = 1$, and $L = 256$ for different diffusion constants $D = 0,100,1000$. In the simulation with $D = 0$ an infinite reaction rate has been used as soon as A and B are nearest-neighbors. ω is given in arbitrary units for comparison reasons.
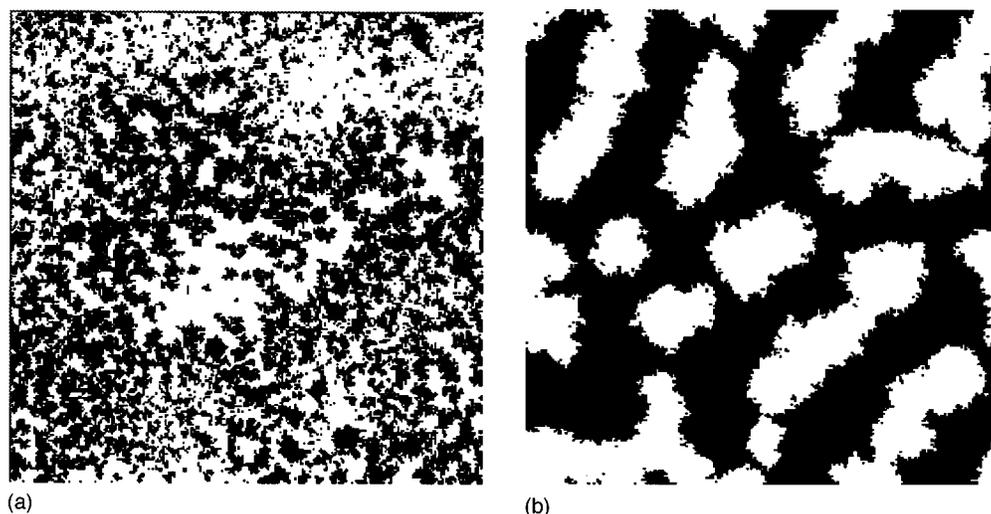
(a)   (b)

FIG. 6. Snapshots of the lattice phases α (black) and β (white) for Pt(100) (left) and Pt(110) (right) with $L=256$, $y=0.49$, $D=100$, $V=1$, and $k=0.1$.

is always smaller than the percolation probability on the square lattice. Therefore we always have small mesoscopic α islands in a macroscopic β phase (or vice versa). For example, in the case of small α phase islands these do not grow to a macroscopic scale which would result in an infinite phase of the α phase and small β phase islands within. Therefore only an infinite matrix of the β phase and small islands of order l of the α phase exist. Fast diffusion is able to partly synchronize these separated α domains. A presentation of the phase distribution on the lattice is given in Fig. 6 where two snapshots are shown. These snapshots which are taken from the simulation show the strong structural dependence on the properties of the reconstructed surface phases. On Pt(100) with very small and hence negligible values of s_α the α islands are highly dispersed, whereas on Pt(110) with larger values of s_α (e.g., $s_\alpha=0.5$) they are denser and almost homogeneous. More important, the phase coverage on Pt(110) changes from a macroscopic α phase with β islands embedded to a macroscopic β phase with embedded α islands. On Pt(110) the surface phases build macroscopic spatio-temporal structures such as target patterns and spiral waves,[30] whereas in the simulations for Pt(100) no such structures occur in correspondence with experimental results. The size of these patterns depends on the A diffusion rate as has also been shown recently by Gelten *et al.*[23] On Pt(110) the same diffusion constant leads to a much larger synchronization length as compared with the case of the Pt(100) surface. But even this synchronization length is finite and much too small to lead to globally synchronized oscillations on length scales of $L=10^7$ which corresponds to the mm range on real catalysts. In this case a second synchronization mechanism must be present which is almost independent of the system size.

IV. CONCLUSION

In this study we investigated in detail a model for the description of kinetic oscillations in catalytic reactions on reconstructing surfaces. In the special case of the catalytic CO oxidation on Pt(100) and Pt(110) oscillations can be ob-

served in all macroscopic variables for $0<y<y_c$ with $y_c=y_c(D,V,k)$. The parameters V, k, and D determine the frequency of the oscillations, which increases as $\omega_0 \sim k\sqrt{V/D}$. The critical CO coverge for the process of the surface reconstruction is determined to $\Theta_{\rm crit}\approx0.293$ as a *result* of the model in qualitative agreement with experimental values. The surface diffusion given by D is able to synchronize the oscillations in a surface domain of size l. Because l increases with increasing D the lattice side length L as an intrinsic parameter of the simulation method rules the global behavior. For $l>L$ the system shows globally synchronized oscillations, whereas for $l<L$ only local oscillations occur, which can interfere and cancel each other. Therefore our model is able to explain some of the most important experimental results such as critical coverages, local oscillations, synchronization mechanisms, and the resulting transition into the limit cycle. These synchronizations are based on fast diffusion which has been neglected or underrated in most other simulations of oscillating surface reactions.

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