

Nucleation and Island Growth Kinetics on Reconstructing Surfaces

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A microscopic lattice gas model for the reconstruction of single crystal surfaces is studied by means of Monte Carlo simulations. The nucleation and growth of the individual surface phases as well as the critical properties which are connected with these processes can thereby be understood. The homogeneous nucleation is the origin of surface phase defects. These defects can grow to a mesoscopic size due to local fluctuations in the adsorbate coverage which are based on the diffusion of the adsorbate.

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Surface structural phase changes induced by the presence of certain adsorbates (e.g., CO or NO) have been observed in numerous experimental investigations and are well known nowadays. Especially the lifting of the surface reconstruction of Pt(100) and Pt(110) by adsorbed CO has been investigated in great detail [1–5]. In this context there coexist different kinetical phenomena, which are observed in experiments: the nucleation and the growth of the individual surface phase domains and the critical adsorbate coverage which is necessary to induce the phase transition. But the origin of these phenomena and the connection between the nucleation/growth processes and the critical coverage remains unclear, because to date, growth rate measurements have been carried out only on a macroscopic length scale. To the best of our knowledge, nucleation rate measurements have not yet been performed. Moreover, studies with contradictory results for the type of the nucleation process (homogeneous [1] or heterogeneous [5]) exist in the literature. For the interpretation of the experiments many assumptions and numerical fits have to be made and the results are thus not yet conclusive. Especially the assumption of almost static local coverages and concerted many-particle processes, where up to six adsorbate particles and eight surface atoms shall be involved [4–6], seems highly improbable. The clarification of the microscopic processes of nucleation and growth of the individual surface phases is of crucial importance because the surface reconstruction is the basic underlying process of all the complex and fascinating phenomena in surface reactions, e.g., periodic and aperiodic kinetic oscillations, the synchronization of these, and the occurrence of chaotical behavior [7]. In this Letter we show for the first time that the phenomena mentioned above are closely connected with each other in the general context of critical phenomena. We show that the nucleation is a homogeneous process. Even more important, we show that fluctuations due to adsorbate diffusion are the basic reason for the growth of the individual surface phases and that these dynamic microscopic terms are the origin of the critical coverages.

The critical CO coverage $\Theta_{\text{CO,crit}}$ for the surface phase transition determines the stability of the different phases.

For $\Theta_{\text{CO}} < \Theta_{\text{CO,crit}}$ only the reconstructed surface phase (α phase) is stable. For $\Theta_{\text{CO}} > \Theta_{\text{CO,crit}}$ the reconstruction is lifted and the nonreconstructed surface phase (β phase) is stable. For Pt(110) $\Theta_{\text{CO,crit}} \approx 0.2$ holds where the α and β phases correspond to the 1×2 and 1×1 surface phases of Pt(110), respectively [7]. For the hex $\rightleftharpoons 1 \times 1$ ($\alpha \rightleftharpoons \beta$) phase transition on Pt(100) the value of the critical coverage has been determined to $\Theta_{\text{CO,crit}} \approx 0.3$ [2,3]. This critical coverage is of macroscopic nature and has been used as an additional parameter without any further explanation in theoretical investigations of the oscillating CO oxidation on Pt single crystal surfaces in the past. Thereby the microscopic reasons for this critical coverage are obscured.

Independent of the macroscopic critical coverages there exist the results for island growth dynamics in adsorbate induced surface reconstruction by Hopkinson and co-workers [4,5]. It was stated that the growth rate r_g of the 1×1 surface phase on Pt(100) obeys a power law $r_g \propto \Theta_{\text{CO}}^\nu$ with an exponent of $\nu = 4.5 \pm 0.4$ with respect to the CO coverage on the hex phase [4]. The exponent ν was said to be within experimental errors, although there is a tendency of an increase in ν with increasing temperature T ($\nu = 3.9, 4.7, 5.4,$ and 5.8 for $T = 380, 390, 400,$ and 410 K, respectively [5]). Hopkinson *et al.* conclude from their molecular beam studies that the nucleation is heterogeneous and that four or five CO molecules are involved in a concerted reaction step resulting in the growth of the 1×1 phase.

Of equal importance to the discussion of nucleation and growth of surface phase domains are the scanning tunneling microscopy results of Ritter *et al.* [1], where it was concluded that the hex $\rightarrow 1 \times 1$ phase transformation is homogeneously nucleated because the growing 1×1 islands were distributed randomly over a terrace without preferential growth from a monatomic step that was imaged on the initial hex surface.

In this Letter we show that our model can explain the experimentally observed nonlinearities. Furthermore, we demonstrate that an apparent heterogeneous nucleation in the experiment can be the result of a purely homogeneous

nucleation on the microscopic (atomic) length scale. Our microscopic model for the nucleation and growth processes has been introduced in Ref. [8] as a simplified version of our model for oscillating surface reactions on single crystal surfaces [9,10]. The present model for the nucleation and growth processes is a simplified theoretical model which does not require any parameters taken from experiment. This is a decisive advantage. We consider a model of Markovian type; i.e., the model is defined by its state variables and the transitions which can occur. We use the regular square lattice with the lattice constant $a = 1$ as a model for the surface of the catalyst. The consideration of different surface geometries seems to be unnecessary because simulations on the triangular lattice give almost the same results. Each individual site can be vacant or covered with A , where A stands for an adsorbate which induces the phase transition (e.g., CO). In addition, each site belongs to the reconstructed (α) phase or the nonreconstructed (β) phase, respectively. In our model all elementary processes are defined locally; i.e., only transitions which change the state of only one or two nearest neighbor (NN) lattice sites can occur. Each transition has a clear physical meaning and is connected with a transition rate of dimension t^{-1} . In the present study we consider a lattice with a constant coverage Θ_A of A ; i.e., we neglect further adsorption, desorption, or reaction processes which obviously occur in real surface reaction systems. In this model system only the surface diffusion of A , the spontaneous homogeneous nucleation of phase defects, and the surface phase propagation (growth process) are considered. Therefore we deal with a closed system with constant coverage of A . These simplifications do not have a large influence on the results presented below. The consideration of the adsorption and desorption of A for the different phases, which would lead to an open system, results in four additional free parameters and leads only to weak fluctuations of the value of Θ_A . The individual transitions are modeled as follows. A particle A can diffuse via hopping from its present site to a vacant nearest neighbor site with the diffusion rate D independent of the phase the sites belong to. The nucleation process occurs with rate γ . In this process the surface phase state of one lattice site is changed spontaneously from the α to the β state or vice versa, completely independently of the coverage of the site and the coverage or the phase state of the neighboring sites. Therefore the nucleation is modeled as a homogeneous process. This nucleation can be accounted for as the result of thermal motion in the upper layer of the surface. The propagation of the borders of the individual phase domains, i.e., the growth process, depends on the presence or absence of A directly at the phase border. Consider a pair of NN lattice sites with one site in the α state and the other one in the β state. If at least one particle A is present on one of the two sites the growth of the β phase occurs with rate V . In this case the site in the α state is changed to the β state. If no A is present the growth of the α phase occurs with the same rate V

and both lattice sites belong to the α phase. The growth of the β phase arising from the presence of A (CO) at the phase border is the consequence of the larger adsorption energy of A (CO) on the β (1×1) compared to the α (hex) phase, which is the experimental fact. The model is simulated by means of Monte Carlo simulations. In the present study we use $D = 100$, $\gamma = 10^{-3}$, and $V = 1$ as standard values because diffusion is by far the fastest process and the nucleation is a rare event. A variation of the parameters with these auxiliary conditions maintained does not lead to qualitative different results. We first deal with the coverages which determine the stability of the individual surface phases, then investigate the nucleation process, and turn finally to the influence of an anisotropy in the diffusion process. It has been shown in Ref. [8] that a model even more simplified than the one discussed here and which includes only A diffusion and the surface phase propagation but neglects the nucleation gives the global critical adsorbate coverage as a result of the model in qualitative agreement with experimental results. In this study the nucleation can be neglected because a heterogeneous phase distribution has been used as the initial lattice condition. There exist three different solutions in different intervals of the A coverage Θ_A as the only parameter. (i) A stable homogeneous α phase ($\Theta_\alpha = 1$, $\Theta_\beta = 0$) exists for $0 < \Theta_A < \Theta_A^{(1)}$ and (ii) a stable homogeneous β phase ($\Theta_\alpha = 0$, $\Theta_\beta = 1$) exists for $\Theta_A^{(2)} < \Theta_A < 1$. In the third interval $\Theta_A^{(1)} < \Theta_A < \Theta_A^{(2)}$ the system exhibits a dynamically stable heterogeneous state where individual domains of the α and β phase coexist on the lattice. The two critical values which can also be seen in Fig. 1 coincide in the limit $V/D \rightarrow 0$ to $\Theta_A^{(1)} = \Theta_A^{(2)} = 1 - 1/\sqrt{2} \approx 0.293$. This result has been confirmed by Monte Carlo simulations [8]. From this model no information can be obtained about the stability of the homogeneous phases in the intervals (i) and (ii) because the phase coverages are constant and equal to unity.

In the present study we additionally consider the homogeneous phase nucleation. This then leads to the kinetic order parameter of the surface phase border propagation. Consider the lattice in the homogeneous β phase with $\Theta_\beta = 1$ and $\Theta_A < \Theta_A^{(1)}$. In this case the β phase is unstable and even a small α defect (i.e., one single site in the α phase) can become macroscopic via phase border propagation. Therefore the almost homogeneous β phase is changed into a homogeneous α phase. The α phase islands grow approximately circular in shape with an effective phase border propagation velocity, v_{\max} , which is independent of the radius of the island for sufficiently long times t . Therefore the number of sites in the α phase, N_α , increases in the phase islands as $N_\alpha \propto \pi v_{\max}^2 t^2$. The same holds for the growth of a β nucleus in a homogeneous α phase for $\Theta_A > \Theta_A^{(2)}$. We have to mention that v_{\max} should depend on Θ_A , V , and D . But in the limit of infinitely fast diffusion, $D \rightarrow \infty$, the parameter D is

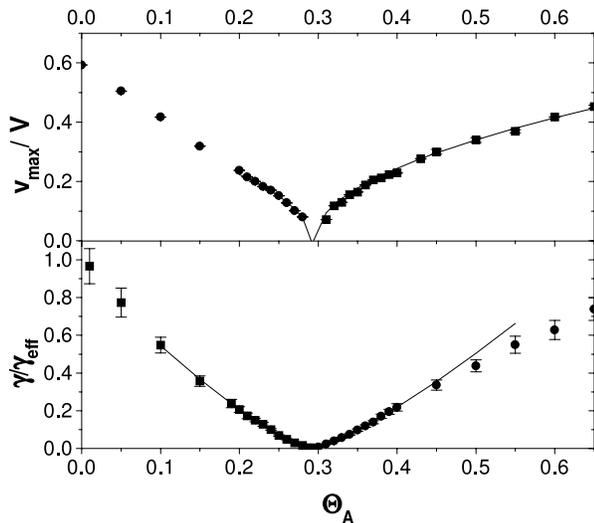


FIG. 1. The ratio v_{\max}/V of the phase propagation velocity v_{\max} and the transition rate V of the phase propagation (top) and the ratio $\gamma/\gamma_{\text{eff}}$ of the nucleation rate γ and the effective nucleation rate γ_{eff} (bottom) are shown for α (circles) and β nuclei (squares) as a function of Θ_A . The error bars give the mean square deviations of the simulation result.

removed and we get the dimensionless variable v_{\max}/V as a function of the A coverage, $v_{\max}/V = f(\Theta_A)$. For finite but very small values of V/D the differences to the case of infinitely fast diffusion ($V/D \rightarrow 0$) should be negligible. This can also be seen in the values of the critical coverages. The two values do not coincide at $\Theta_A^{(1)} = \Theta_A^{(2)} = 1 - 1/\sqrt{2} \approx 0.293$ as shown above for $V/D \rightarrow 0$ but show slightly different values of $\Theta_A^{(1)} \approx 0.291$ and $\Theta_A^{(2)} \approx 0.294$ for the ratio $V/D = 0.01$ which is used in this Letter. In Fig. 1 the values of the ratio v_{\max}/V as the kinetic order parameter are shown as a function of Θ_A . The maximum of $v_{\max}/V \approx 0.59$ is reached for the limits $\Theta_A \rightarrow 0$ and $\Theta_A \rightarrow 1$ of the A coverage. We define the variable ε as

$$\varepsilon = \frac{\Theta_A^{(1)} - \Theta_A}{\Theta_A^{(1)}} \quad \text{for } \Theta_A < \Theta_A^{(1)} \quad (1)$$

and

$$\varepsilon = \frac{\Theta_A - \Theta_A^{(2)}}{1 - \Theta_A^{(2)}} \quad \text{for } \Theta_A > \Theta_A^{(2)}. \quad (2)$$

A nonlinear curve fitting of 10 data points near the critical points gives in both cases the dependence

$$\frac{v_{\max}}{V} \propto \varepsilon^x \quad (3)$$

with $x = 0.54 \pm 0.02$ for $\Theta_A < \Theta_A^{(1)}$ and $x = 0.54 \pm 0.03$ for $\Theta_A > \Theta_A^{(2)}$; i.e., we approximately obtain a parabolic dependence ($x = 1/2$).

Next we consider the nucleation process with rate $\gamma > 0$. In a system with no chemical coverage ($\Theta_A = 0$) the

nucleation leads only to one-point β defects in a macroscopic α phase. These defects are then quickly erased via the phase border propagation. The average density of the β defects can be obtained from the equation $d\Theta_\beta/dt = \gamma - V\Theta_\beta$ which leads to the induced coverage $\Theta_\beta^{\text{ind}} = \gamma/V$ in the steady state. The same holds for α defects in a macroscopic β phase with a completely covered surface, i.e., $\Theta_\alpha^{\text{ind}} = \gamma/V$ for $\Theta_A = 1$. Therefore a coverage $\Theta_A > 0$ of A supports the nucleation in such a way that even small nuclei can grow to a mesoscopic size because of local fluctuations in the chemical coverage. The size and the lifetime of these nuclei increase with increasing fluctuations. But the nucleation with rate $\gamma > 0$ is essential for the formation of mesoscopic nuclei because it creates the initial surface phase defects.

For small values of γ the density of $\Theta_\beta^{\text{ind}}$ (or $\Theta_\alpha^{\text{ind}}$) is proportional to γ . Therefore the dimensionless variable $\Theta_\beta^{\text{ind}}$ shows the dependence $\Theta_\beta^{\text{ind}} = \frac{\gamma}{V}\xi(\Theta_A)$. Note that this holds formally only in the limit of infinitely fast diffusion, $D \rightarrow \infty$, but can be used as a very good approximation for fast but finite diffusion (see above). $\xi(\Theta_A)$ is a function of the chemical coverage which describes an effective amplification of the formation of the individual phase nuclei. We now define the effective nucleation rates $\gamma_{\text{eff}} = V\Theta_\beta^{\text{ind}} = \gamma\xi(\Theta_A)$ and $\gamma_{\text{eff}} = V\Theta_\alpha^{\text{ind}} = \gamma\xi(\Theta_A)$ for the β and α nuclei, respectively.

In Fig. 1 the ratio of $\gamma/\gamma_{\text{eff}} = \xi^{-1}(\Theta_A)$ is shown. In the range of the critical coverages of adsorbate A this ratio shows an exponential dependence on ε as

$$\frac{\gamma}{\gamma_{\text{eff}}} = \varepsilon^y. \quad (4)$$

The nonlinear curve fit of 10 points in the neighborhood of the critical coverages leads to $y = 1.30 \pm 0.03$ and $y = 1.26 \pm 0.02$ for $\Theta_A < \Theta_A^{(1)}$ and $\Theta_A > \Theta_A^{(2)}$, respectively. Therefore the effective nucleation rate obtains as $\gamma_{\text{eff}} = \gamma\varepsilon^{-y}$.

There obviously exists a similarity to the theory of ferromagnetism. In this case a weak external field induces a magnetization in the paramagnetic domain and the ratio of these, the susceptibility, diverges at the critical point. In our case the weak nucleation as an internal process plays the same role as the external field in the case of the induced magnetization.

A direct comparison of the above results of our simple model with experimental results is impossible, of course. In real surface reactions there are many additional phenomena such as mass transport of surface atoms, surface roughening because of the different geometries, and densities of the individual phases and energetic interactions between the adsorbates and the surface. These microscopic details form a largely unknown territory. Even the experimentally observed macroscopic critical coverages are only approximately known to within one significant figure. But some points can be mentioned with respect to

experiment. The value of $\gamma_{\text{eff}} \propto \varepsilon^{-\nu}$ increases very fast when Θ_A approaches the critical values ($\varepsilon \rightarrow 0$). Therefore it is possible to fit the function $\gamma_{\text{eff}} = \gamma \xi(\Theta_A)$ with a nonlinear term Θ_A^ν in a certain interval. The value of the exponent ν depends on the interval of Θ_A for which γ_{eff} is fitted. At first sight this seems to be a contradiction to experiment because in Refs. [4,5] it has been shown that the island growth rate depends on the local CO coverage on the hex phase but is virtually independent of the total CO coverage. But note that the model presented here is only a very basic model for surface reconstruction. Especially the neglect of different physical properties of the individual surface phases hinders the investigation of the influence of local coverages because in the model presented above the local coverages on the two phases are equal to the total coverage. But there is a remedy. The introduction of membranelike diffusion splits the critical point into two individual critical points and our model can be fitted to the experimental results given in Refs. [4,5]. For this we define an anisotropy in the diffusion parameter $\kappa = (D_{\alpha\beta} - D_{\beta\alpha}) / (D_{\alpha\beta} + D_{\beta\alpha})$ which considers the diffusion rates $D_{\alpha\beta} = D(1 + \kappa)$ [$D_{\beta\alpha} = D(1 - \kappa)$] for the hopping from the α [β] to the β [α] phase (with $D_{\alpha\alpha} = D_{\beta\beta} = D$). In this way we account indirectly for the larger adsorption energy of A particles on the β phase. For $\kappa = 0.93$ we get two local critical values $\Theta_A^{(1)} = 0.033$ and $\Theta_A^{(2)} = 0.483$ in very good agreement with experimental results [4,5]. Now the effective nucleation rate γ_{eff} can be fitted as a function of the local CO coverage $\Theta_A^{(\alpha)}$ on the α phase. For $\kappa = 0.93$ we get $\gamma_{\text{eff}}/\gamma \propto [\Theta_A^{(\alpha)}]^\nu$ with $\nu = 6.51 \pm 0.58$ as shown in Fig. 2. This nonlinearity is not based on nonlinear reaction orders but originates from cooperative processes which occur in the vicinity to the critical points.

In addition, one has to consider that the parameter γ_{eff} characterizes the state of the surface and can be interpreted as a parameter for the surface activity. It seems probable that certain experimental methods such as molecular beam studies may influence strongly this activity because the adsorbate coverage is changed very quickly. Furthermore, the homogeneous nucleation of surface phase defects seems probable because of the thermal motion of the surface atoms, at least with the small nucleation rates which are used in our present study. These defects can grow to a mesoscopic size only if the local A coverage is sufficiently large due to fluctuations. Otherwise the defects are erased via the phase border propagation. In experiments only nuclei of a certain size can be observed. Because these do exist only in domains with a large local adsorbate coverage, the nucleation may appear to be heterogeneous.

In summary, our model which focuses on the essential processes for the surface reconstruction is able to explain the basic microscopic mechanism thereof. Homogeneous

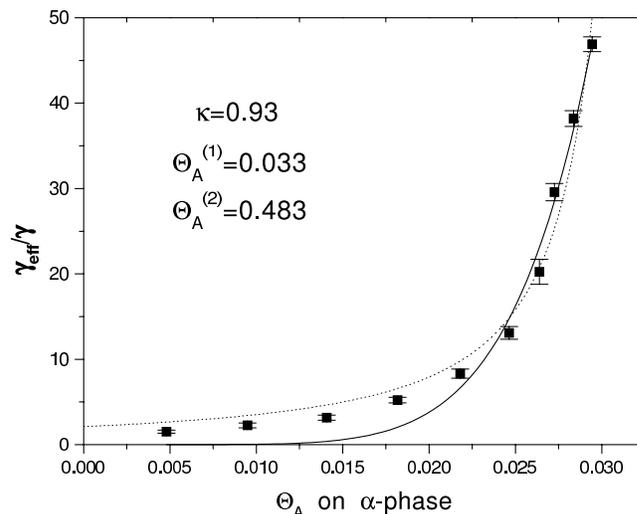


FIG. 2. The ratio $\gamma_{\text{eff}}/\gamma$ of the nucleation rate γ and the effective nucleation rate γ_{eff} is shown as a function of the local CO coverage on the α phase. The error bars give the mean square deviations of the simulation results (squares). The lines show the fit to $\gamma_{\text{eff}}/\gamma \propto [\Theta_A^{(\alpha)}]^\nu$ with $\nu = 6.51 \pm 0.58$ (solid line) and to $\gamma_{\text{eff}}/\gamma \propto \varepsilon^{-x}$ with $x = 1.42 \pm 0.11$ (dotted line).

phase nucleation is the essential process. The resulting nuclei can grow to mesoscopic sizes via fluctuations in the local A coverage. Thus for the first time this mechanism can be brought to light which has remained obscure because experiments by their very nature mix a lot of individual processes. This renders an analysis very difficult. The critical and nonlinear properties well known from real systems with surface reconstruction are a result of the present model.

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