Comment on "Surface restructuring, kinetic oscillations, and chaos in heterogeneous catalytic reactions"

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In a recent article Zhdanov studied the oscillating $NO + H_2$ reaction on the Pt(100) single-crystal surface [V. P. Zhdanov, Phys. Rev. E **59**, 6292 (1999)]. We have scrutinized his model and found fundamental errors in the chemical modeling, in the modeling of the surface reconstruction and in the simulation procedure itself.

I. INTRODUCTION

"Critical phenomena occurring in adsorbed overlayers at conditions far from equilibrium are of high current interest. To simulate such phenomena, one inevitably needs to employ a series of assumptions and simplifications, which should of course reflect the main properties of a system under consideration. The recent paper proposed by Khrustova, Veser, Mikhailov, and Imbihl [1], treating the chaotic kinetics of the NO-CO reaction on Pt(100), does not seem to satisfy the latter requirement." With these introducing sentences Zhdanov began a comment [2] on a surface reaction model of the authors mentioned above [1]. We think that especially the statement that such models should "reflect the main properties of a system under consideration" is of paramount importance and is violated or even completely neglected in the very model proposed by Zhdanov.

Zhdanov [3] claims his model to be a decisive improvement in the context of microscopic models for oscillating reactions on reconstructing surfaces which are investigated by means of Monte Carlo (MC) simulations. In his opinion in "all the available MC models, the pure mathematical rules employed to realize the steps related to surface restructuring are far from those prescribed by statistical mechanics." Zhdanov used this model in a series of studies on different surface reactions [4–6].

In this comment we discuss his model in detail and show that the definition of the model is wrong at a fundamental level and that it contradicts important experimental results which have been obtained in studies explicitly dealing with surface reconstruction. In addition we give an alternative model which is able to explain the process of surface reconstruction very easily in agreement with experimental results.

II. CHEMISTRY OF THE NO+H_2 REACTION

A. Selection rule

The kinetic scheme initially given by Zhdanov includes seven steps from which two steps are as stated not elementary steps on the microscopic length scale but are composed of 2 and 3 microscopic substeps, respectively (H_2O and NH_3 formation). The whole reaction scheme therefore has 10 microscopic elementary reaction processes in which eight adsorbate species occur. This kinetic scheme is then compressed to a simplistic one consisting of one reaction step from the original scheme (NO adsorption and desorption) and one new artificial reaction step (NO decomposition, i.e., its transformation into a vacant lattice site because both products of dissociation are immediately neglected) with NO as the only adsorbate species. The applied reaction scheme thus is

$$NO_{gas} + * \rightleftharpoons NO_{ads},$$

$$NO_{ads} + * \rightarrow 2*,$$
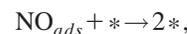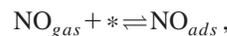
where $*$ stands for a vacant lattice site and the indices *gas* and *ads* mean a particle in the gas phase or adsorbed onto the surface, respectively. This model has been justified as follows: (1.1) The macroscopic production rate is small for N_2O, the rate of NH_3 formation is lower than that of N_2 desorption and (1.2) the steps resulting in H_2O formation and the desorption of N_2 are very fast.

B. Comments

In the context of a microscopic model the arguments given by Zhdanov are rather peculiar and the resulting model has nothing in common with a chemically and physically reasonable model for the $NO + H_2$ reaction on Pt(100). A consequence of this model of a nonreaction is that all systems with a dissociative adsorption should show the same nonlinear phenomena which is not true. The individual reaction steps are arbitrarily ruled out because the reaction rates of these steps are either small or large, respectively. For this we first give a counter-example against argument (1.1): Jansen and Nieminen [7] showed that a nonreacting adsorbate can induce oscillations simply because of its presence on the surface, i.e., a nonreacting species completely changes the kinetics of their model system. Therefore, the argument that a reaction step can be neglected because of its small macroscopic reaction rate does not hold. Even more peculiar is the neglect of just this N_2 desorption because it is rather fast. (1.2) In this context one has to distinguish between reactions

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which are fast at the macroscopic or the microscopic level, respectively. If a reaction is fast at the macroscopic level a microscopic model must be able to explain this phenomenon and the conditions under which this macroscopically fast reaction can occur. If the reaction step is fast at the microscopic level this argument is simply void. This can be clearly seen in the pioneering model by Ziff, Gulari, and Barshad [8] or the NO+CO reaction model [9,10] where the microscopic reactions are infinitely fast. The macroscopic reaction rates remain finite and even can become very small because of segregation of the adsorbate species or the existence of special adsorbate structures. The reason for this is that the macroscopic reaction rate is given by the product of the microscopic transition rate and the probability to find a pair of reacting particles on nearest-neighbor (NN) sites, i.e., the macroscopic production rate depends on the structures which are built in the adsorbate layer. E.g., in the NO+CO reaction the N atoms build a checkerboard superstructure [9,11–13] and the macroscopic N+N reaction (N_2 desorption) does not occur, although the microscopic transition rate is infinite for this step.

III. MODELING OF THE SURFACE RECONSTRUCTION

A. General remarks

The coexistence of two different structures or surface phases with different adsorbate coverages on Pt(100) exhibits a certain similarity with the coexistence of individual phases during a first-order phase transition (FOPT), e.g., the melting of ice. But the conclusion that ''the adsorbate-induced reconstruction on the (100) face of Pt should be described in terms of the theory of first-order phase transitions'' is not correct. There may be other reasons for the mentioned similarity (see below, our alternative). All models for surface reconstruction which are based on the theory of FOPT's have one decisive disadvantage: They predict a complete segregation of the phases, completely independent of their specific definition. The large phase islands grow at the expense of the smaller ones. This has also been confirmed by Zhdanov himself. He showed in a MC study [6] that the mean size of the islands occurring in his model for surface reconstruction obeys the well-known law by Lifshitz-Slyoznov. In real systems this phase segregation does not occur as has been shown in numerous beautiful experimental studies which have been performed mainly by the group of Ertl [14]. Two structures coexist on the surface in a dynamically stable heterogeneous state. Therefore not only the results but even the definition of the model by Zhdanov directly contradicts experimental observations. A further contradiction to experimental results follows from the definition in terms of the theory of FOPT's. The experimentally observed critical behavior of the nonlinear island growth rate which has been observed by Hopkinson *et al.* [15,16] cannot be explained with a FOPT because it does not show such a critical behavior in the vicinity of the critical points.

On Pt(100) the 1×1 (β) surface structure is preferred if the local coverage of certain adsorbates (e.g., CO or NO) is larger than a certain critical coverage. Otherwise the *hex* (α) structure is preferred. This also holds for a clean surface. In

real systems the β phase has a dense adsorbate coverage whereas the adsorbate coverage on the α phase is small. Zhdanov draws the conclusion that the desorption rate should be large on the α phase and very small on the β phase. But this conclusion cannot be drawn because again other processes can be the origin for the difference in the coverages of the different surface structures (see below, our alternative). In the following analysis of the model proposed by Zhdanov we consider a system without reaction, i.e., we neglect the decomposition of NO and therefore concentrate only on the surface reconstruction because of the presence of an appropriate adsorbate such as NO.

B. Modeling

The model has four free energetic parameters, the metal-metal (ϵ_{MM}), the adsorbate-metal (ϵ_{AM}), the adsorbate-adsorbate (ϵ_{AA}) interaction, and the energy difference ΔE between a metal atom in the metastable (β) and in the stable (α) state, respectively. The values $\Delta E/k_B T=2$, $\epsilon_{MM}/k_B T=0.5$, $\epsilon_{AM}/k_B T=2$, and $\epsilon_{AA}/k_B T=0$ are stated as standard values for surface reconstruction [3]. It is important to note that the energetic interactions on the atomic length scale are almost unknown. In the following we use the values given above as well as the assumption that in a homogeneous surface structure each site has 4 NN sites in the same surface state. Furthermore, at the border of the surface structures we consider 3 NN surface sites in the same surface state and one site in the other state (linear border). These assumptions are not restrictive because other conditions at the surface border can be investigated in an analogous way. The model in Ref. [3] has the following properties.

(2.1) *Anomalous ratio of the desorption rates*. The desorption rates $k_{des}^{(\chi)}$ with $\chi=\alpha,\beta$ on the homogeneous α and β phase differ by four orders of magnitude: $k_{des}^{(\beta)}/k_{des}^{(\alpha)}=W$ $=\exp(-4\epsilon_{AM}/k_B T)\sim10^{-4}$. Therefore, the β phase is almost completely covered by NO at the rates for adsorption used in the study by Zhdanov.

(2.2) *Asymmetric adsorbate diffusion at the phase border*. The jumps of adsorbate particles from the β to the α phase are strongly hindered and the ratio of these is $D_{\beta\alpha}/D_{\alpha\beta}$ $=W'=\exp(-2\epsilon_{AM}/k_B T)\sim10^{-2}$. The diffusion on the homogeneous structures is not affected by the applied rules.

(2.3) *Large nucleation rate of the β phase*. Let us consider the unstable state of a homogeneous *alpha* phase completely covered by adsorbate A (e.g., NO). A local nucleation process $\alpha\rightarrow\beta$, i.e., the formation of a local phase defect, is connected with the sum of all interactions $\mathcal{E}_{\alpha\beta}=\Delta E$ $+8\epsilon_{MM}-4\epsilon_{AM}$. For the nucleation of an α defect in a clean homogeneous β phase, $\beta\rightarrow\alpha$, the difference in the energies is given by $\mathcal{E}_{\beta\alpha}=-\Delta E+8\epsilon_{MM}$. The corresponding Boltzmann factors are $W_{\alpha\beta}=\exp(-\mathcal{E}_{\alpha\beta}/k_B T)\sim10$ and $W_{\beta\alpha}$ $=\exp(-\mathcal{E}_{\beta\alpha}/k_B T)\sim0.1$, i.e., the nucleation is defined asymmetrically and is very fast on the α phase and slow on the β phase. The nucleation rates on both phases differ by about two orders of magnitude.

(2.4) *Asymmetric phase border propagation*. In the model described by Zhdanov the nucleation and the growth (i.e., the phase border propagation $\alpha\beta\rightarrow\alpha\alpha$ or $\alpha\beta\rightarrow\beta\beta$ for NN

sites) are defined via the same rules. On a surface which is completely covered by an adsorbate or empty $\mathcal{E}'_{\alpha\beta}=\Delta E +4\epsilon_{MM}-4\epsilon_{AM}$ or $\mathcal{E}'_{\beta\alpha}=-\Delta E +4\epsilon_{MM}$ hold for the sums of all interactions, respectively. Again, the rules are defined asymmetrically in favor of the formation of the β phase with the corresponding Boltzmann factors $W'_{\alpha\beta}\sim 10^2$ and $W'_{\beta\alpha}=1$, i.e., again both rates differ by about two orders of magnitude.

C. Comments

The author wants to introduce a driving force for the phase separation into his model. But due to the definition of the model *all* of the above-mentioned processes (2.1)–(2.4) are partly responsible for the phase separation. This hinders an analysis of the model because in this case all processes are in part responsible for any phenomenon which occurs.

The processes (2.1) and (2.2) are combined in the author's model because both processes are determined by the value of the parameter ϵ_{AM}. But there is no reason for this forced combination of both processes. Moreover, it is physically not reasonable. An adsorbate particle on the surface is subject to different potentials on the surface. In particular there are potentials perpendicular to the surface (adsorption and desorption) and potentials parallel to the surface (diffusion). Therefore, the adsorption and desorption process (2.1) and the diffusion process (2.2) should be governed by different parameters. Let us elaborate a simple example to clarify this point. Consider an almost homogeneous surface structure with large terraces and only a few ideal steps. The individual terraces can be regarded as different ''phases.'' The desorption is then completely independent of the phase, $W=1$, but in the diffusion from one phase to the other there exists an asymmetry, $W'\neq 1$, e.g., the jump one step up may be hindered compared to a jump one step down.

Let us elaborate a further thought experiment for processes (2.3) and (2.4). Consider a homogeneous α phase which is free of adsorbate particles. If we now cover the surface (completely) with adsorbate A via fast A adsorption the α phase gets unstable and the β phase is formed. In the model introduced by Zhdanov this new β phase will be created via a collapse of the α phase because the difference of the Boltzmann factors for the nucleation and for the phase border propagation (island growth) is small $W_{\alpha\beta}/W'_{\alpha\beta}\sim 0.1$. Therefore, the nucleation and the phase border propagation will occur with very similar rates. This is a clear contradiction to the experiment where it has been shown that the nucleation is a very rare process and that the defects once nucleated can grow to very large islands before they combine with other phase islands [17]. This is the well established nucleation and growth mechanism [14]. A further point is that the rates of adsorption and nucleation in Ref. [3] are of the same order of magnitude and are coupled because of the definition of the model. This is a further contradiction to experiment where it has been shown that both processes are decoupled [18]. In the latter study the nucleation proceeds for several minutes although the coverage has reached a constant value. Therefore a separation between these two processes should exist due to very different rates, i.e., the ad-

sorption should be very fast compared to the nucleation process.

IV. SIMULATION

A. Algorithm of the simulation

The simulation procedure performed by Zhdanov is as follows. (3.1) The time is measured in so-called Monte Carlo steps (MCS). (3.2) The processes are divided into groups on account of their relative weights. In each group there exist additional divisions with additional weights. (3.3) At the end of this chain the process which occurs is chosen by the Boltzmann factor according to the Metropolis rule. Due to this rule all processes with a Boltzmann factor $W>1$ are set to $W=1$.

B. Comments

A MC simulation which contains kinetic parameters is always connected with the corresponding master equation via the constant kinetic transition rates for the elementary microscopic reaction processes. These transition rates give an unequivocal definition of the time scale and the probabilities for the MC simulation procedure [19–21]. This is missing in the author's model. Even worse is the use of the Metropolis rule because this rule can only be applied to systems approaching the thermodynamic equilibrium. A system which shows kinetic oscillations and chaotical behavior does certainly not belong to this class. Therefore one can only assume which portion of these kinetic phenomena originates directly from the use of the Metropolis rule. It is certainly an arbitrary action to replace Boltzmann factors of $W=10^2$ with the value $W=1$. And it is certainly physically wrong. The author tends to ignore that there exist alternative methods especially for the case where all statistical weights have an upper limit and are embedded in a kinetic environment [22].

V. ALTERNATIVE MODEL FOR SURFACE RECONSTRUCTION

We now shortly sketch that the phase separation can in the simplest way be explained by assuming only the asymmetric adsorbate diffusion between the individual surface phases as a driving force. Our idea can be analyzed very easily in the context of the MF approximation. The results given below have been quantitatively confirmed by MC simulations.

We consider a model system with no reactions and with equal transition rates $k^{(\alpha)}_{\mathrm{des}}=k^{(\beta)}_{\mathrm{des}}=k_{\mathrm{des}}$ for A desorption on both surface phases. Under this condition the *global* saturation coverage of adsorbate A, Θ_A, is independent of the distribution of the surface phases α and β. The *local* adsorbate coverages on the individual phases do not only depend on the global value Θ_A but also on the density of the β (or α) surface phase $\Theta_\beta=\theta$ ($\Theta_\alpha=1-\Theta_\beta$). We now define the state of one lattice site with the chemical variable $X=0,A$ and the phase variable $\chi=\alpha,\beta$. X determines if the site is vacant or covered by A, whereas χ determines the phase the site belongs to. The probability to find a lattice site with

phase χ and covered with X is given by C_X^χ. For this model definition the following sum rules hold:

$$C_A^\alpha + C_A^\beta = \Theta_A,$$

$$C_A^\beta + C_0^\beta = \Theta_\beta = \theta, \tag{1}$$

$$C_A^\alpha + C_0^\alpha = \Theta_\alpha = 1 - \theta.$$

The local A coverage on the χ phase can then be calculated to $\Theta_A^{(\chi)} = C_A^\chi / \Theta_\chi$.

Let us first consider a constant phase distribution, θ = const. In the equilibrium the number of jumps from the α to the β phase is equal to the jumps in the opposite direction,

$$D_{\alpha\beta} C_A^\alpha C_0^\beta = D_{\beta\alpha} C_0^\alpha C_A^\beta. \tag{2}$$

With the introduction of

$$\kappa = \frac{D_{\alpha\beta} - D_{\beta\alpha}}{D_{\alpha\beta} + D_{\beta\alpha}} \in [-1,1] \tag{3}$$

as a dimensionless parameter for the diffusion asymmetry, the phase border now acts like a membrane which supports the jumps of adsorbate particles from one phase to the other and hinders the jumps into the opposite direction. We here use $\kappa = 0.9$ for a strong asymmetry which results in a strong membrane effect.

In Fig. 1 the solution of Eqs. (1) and (2) is shown. It can be clearly seen that for small values of Θ_A (low adsorbate coverage) and θ (only a few small β phase islands) the coverage of the α phase is almost equal to the global coverage but that the coverage on the β phase is almost one order of magnitude larger than that on the α phase. This is in excellent agreement with experimental results [23,24,15,16,14]. Therefore, in our model the membrane effect in the diffusion at the phase border is the only driving force for phase separation. In this context it is important to know which value of θ corresponds to a certain constant value of the adsorbate coverage Θ_A because with increasing θ the difference in the values for the local phase coverages decreases. This value is determined by the two processes of defect nucleation and island growth. In agreement with Zhdanov and previous models [25,7] we use a local description of the transitions, i.e., only the phase and the coverage of NN sites have to be considered and all particles on next-nearest-neighbor sites or at a larger distance do not have any influence. In agreement with Zhdanov we use the presence and absence of an adsorbate particle as the driving force for the growth and decline of the phase islands but in contrast we assume the transition rates to be equal for both phases. Therefore a pair of NN sites in the phase state $\alpha\beta$ transforms into $\alpha\alpha$ ($\beta\beta$) if none (at least one) of the site is covered by A. In equilibrium the number of $\alpha\beta \to \alpha\alpha$ and $\alpha\beta \to \beta\beta$ transitions should be equal, i.e.,

$$C_0^\alpha C_0^\beta = C_A^\alpha C_0^\beta + C_0^\alpha C_A^\beta + C_A^\alpha C_A^\beta. \tag{4}$$

The solution of Eqs. (1) and (4) is also shown in Fig. 1. The two planes for the coverage $\Theta_A^{(\chi)}$ intersect and the corre-
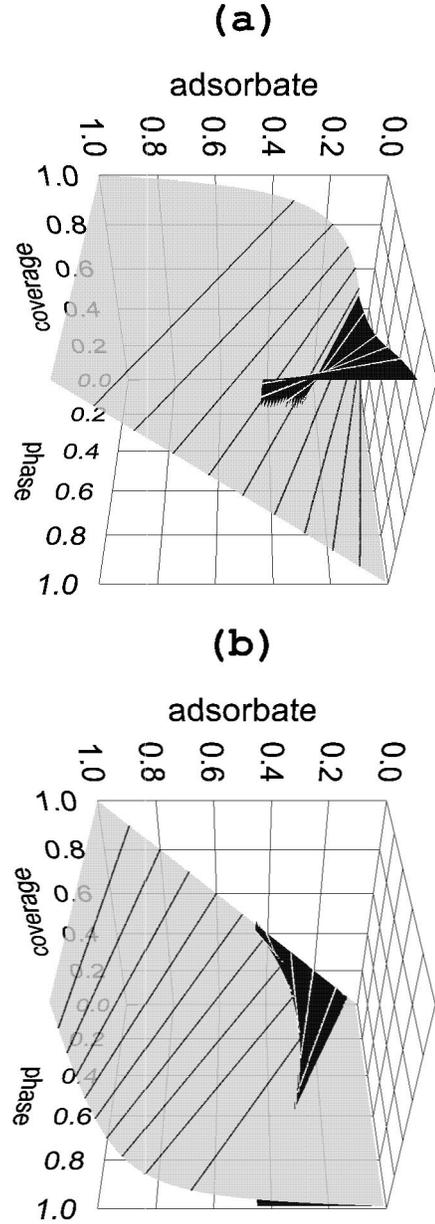

FIG. 1. Phase diagram of the system on the β (a) and the α (b) phase. The solutions of Eqs. (1) and (2) and Eqs. (1) and (4) are given in grey and black, respectively. The axes give the total adsorbate coverage Θ_A (adsorbate), the phase coverage θ (phase), and the local adsorbate coverages $\Theta_A^{(\beta)}$ (a) and $\Theta_A^{(\alpha)}$ (b) (coverage), respectively.

sponding line is parallel to the $\theta - \Theta_A$ plane. The physical interpretation of this is the existence of a dynamically stable heterogeneous state without segregation. In this state the two phases have constant but different local adsorbate coverages given by

$$\Theta_A^{(\alpha)} = \frac{1-\kappa}{2-\kappa+\sqrt{2-\kappa^2}} \tag{5}$$

and

$$\Theta_A^{(\beta)} = \frac{1+\kappa}{2+\kappa+\sqrt{2-\kappa^2}}. \tag{6}$$

This heterogeneous state only exists in the interval $\Theta_A^{(\alpha)} < \Theta_A < \Theta_A^{(\beta)}$, i.e., the system exhibits two critical values for the stability of the two phases. For $\Theta_A < \Theta_A^{(\alpha)}$ ($\Theta_A > \Theta_A^{(\beta)}$) only the homogeneous α (β) phase exists. In the heterogeneous state the coverage of the individual phases can be calculated to

$$\theta = \frac{\Theta_A^{(\beta)} - \Theta_A}{\Theta_A^{(\beta)} - \Theta_A^{(\alpha)}}. \tag{7}$$

E.g., for a relatively strong asymmetry $0.75 < \kappa < 0.95$ we obtain the critical values $0.10 > \Theta_A^{(\alpha)} > 0.02$ and $0.44 < \Theta_A^{(\beta)} < 0.48$ which are in excellent agreement with the (uncertain) experimental values of $\Theta_A^{(1)} \approx 0.05$ and $\Theta_A^{(2)} \approx 0.5$ which are only given with one significant figure [23,24].

A detailed description of our kinetic model can be found in Refs. [20] and [21]. It is able to explain the existence and synchronization of kinetic oscillations and even shows the transition into chaos via the Feigenbaum route [26]. In these studies it was possible to neglect the membrane effect at the phase border because it does only lead to quantitative changes in the critical values but does not alter the oscillations qualitatively. The influence of the homogeneous nucleation and of the membrane effect in the adsorpbate diffusion has been studied in Refs. [27] and [28]. Additional information, lattice snapshots, movies, and a simulation tool are available online [29].

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