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Catalytic reduction of NO with NH_3 on a Pt(100) surface: Monte Carlo simulations

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We propose a surface reaction model for NO reduction with NH_3 on a Pt(100) single crystal catalyst surface and we explore it by carrying out Monte Carlo simulations. Our model includes experimentally observed realistic features such as adsorbate-induced surface phase transition, structure-dependent sticking coefficients and reactivity, desorption probabilities, and surface diffusion of adsorbed species. We discuss similarities found while comparing the available experimental data and our model as reactant ratio and temperature vary. Simulations qualitatively reproduce the kinetic oscillations observed in reaction rates and surface coverages. Also, the essential role of the adsorbate-induced phase transition regarding the appearance of kinetic oscillations is discussed.

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I. INTRODUCTION

The catalytic reduction of nitric oxide with ammonia is an important industrial and environmental process. A better understanding is hence desirable in order to reduce the emissions of NO from power plants and from nitric acid production via the Ostwald process [1]. Besides its practical importance, this reaction system has attracted a great deal of attention because of the interesting dynamical behavior observed. In a series of papers, Imbihl *et al.* have found multiple steady states, kinetic oscillations, and surface phase transitions when the reaction was carried out in a flow reactor under UHV conditions [2–4]. Kinetic oscillations were also observed by Nieuwenhuys *et al.* under similar conditions [5].

The Pt(100) surface is known to exhibit reversible adsorbate-induced phase transitions (AIPT) between two surface structures with different catalytic properties. When a clean Pt(100) surface is exposed the topmost layer atoms move into a reconstructed hexagonal array, i.e., the hex phase. This process can be reverted by adsorption of several molecules (e.g., carbon monoxide, nitric oxide, oxygen) which causes the surface atoms to move back into a bulklike square array, i.e., the 1 × 1 phase [6–8].

Several mechanisms were proposed for the reaction system; among them Lombardo, Fink, and Imbihl (LFI) [2], presented a mechanism that includes seven intermediate adspecies together with experimentally determined rate constants for the elementary processes (the LFI mechanism). Based on their experimental results, Nieuwenhuys *et al.* [5] proposed a different mechanism, with the role of the AIPT being the main difference between them. However, both groups coincide in the opinion that the major products detected under similar conditions are N_2 and H_2O.

The LFI mechanism, in line with molecular beam experiments performed by King *et al.* [9,10], includes a number of realistic features such as lifting of the 1 × 1 phase, which starts when NO coverage on the hex phase overcomes a critical value, inability of the hex phase to adsorb NH_3 and also to dissociate NO, and finally, different NO desorption energies and sticking probabilities on both phases (S_i^j, with i and j representing adsorbate and phase, respectively). Instead, Nieuwenhuys *et al.* consider essential for the appearance of kinetic oscillations an autocatalytic step of decomposition of adsorbed NO.

A number of studies have recently been devoted to perform simulations of the reaction system in the micrometer range using the LFI mechanism. For this purpose mean field (MF) reaction-diffusion equations were used, and a number of features such as the "island growth" mechanism and "site blocking" effect experimentally observed by Imbihl *et al.* [3,11] were successfully reproduced [12–15]. Nevertheless, when using MF equations, details of the adsorbate spatial distribution cannot be followed down to the nanometer scale. For this purpose a suitable method is the Monte Carlo (MC) technique [16–18]. In this work we therefore propose a model for the reaction system and carry out MC simulations. We explored the parameter space for partial pressures and temperature, and compared our results with actual experimental data and previous MF simulation results. Also we examined the influence of the AIPT on the dynamics of the reaction system.

The remainder of this work is organized as follows. In Sec. II we give a brief description of the reaction system and present our reduced Monte Carlo approach to the problem. Section III contains the parameters used in our simulations. In Sec. IV the algorithm used is described, and in Sec. V we summarize and discuss our main results. Conclusions are given in Sec. VI.

II. REACTION SYSTEM

A. Experimental features

Nieuwenhuys *et al.* [5] observed kinetic oscillations in the NH_3+NO reaction on Pt(100) under UHV conditions ($\approx 1 \times 10^{-6}$ mbar), temperature in the range $420\ \mathrm{K} < T < 490\ \mathrm{K}$, and a partial pressure ratio maintained between $0.1 < p_{NO}/p_{NH_3} < 4.3$. They reported that typically, the peaks in

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reaction rate were out of phase with those of NO. Values of the $p_{\mathrm{NO}}/p_{\mathrm{NH}_3}$ ratio above some T-dependent critical range were found to lead to poisoned states, and detailed behavior of the period and amplitude of oscillations was also given.

Imbihl *et al.* [3,2] likewise observed kinetic oscillations in product partial pressures and surface coverages when they explored a similar parameter range, specifically different temperatures and $p_{\mathrm{NO}}/p_{\mathrm{NH}_3}=0.5$ were used. Furthermore, a variety of striking phenomena concerning the surface spatial distribution of adsorbates were reported. As temperature was increased, the authors observed the evolution of the reaction system from nonsynchronized (spatiotemporal turbulence) to synchronized patterns (e.g., spiral waves, island nucleation, and homogenous phase transitions).

Both groups proposed similar Langmuir-Hinshelwood reaction mechanisms consisting of adsorption-reaction-desorption steps that, disregarding the differentiation of hex and 1×1 phases included by Imbihl *et al.* can be written schematically as follows:

$$\mathrm{NO}(g) + * \rightleftharpoons \mathrm{NO}(a), \tag{1}$$

$$\mathrm{NH}_3(g) + * \rightleftharpoons \mathrm{NH}_3(a), \tag{2}$$

$$\mathrm{NH}_3(a) + 3* \rightleftharpoons \mathrm{N}(a) + 3\mathrm{H}(a), \tag{3}$$

$$\mathrm{NO}(a) + * \rightleftharpoons \mathrm{N}(a) + \mathrm{O}(a), \tag{4}$$

$$2\mathrm{N}(a) \rightarrow \mathrm{N}_2(g) + 2*, \tag{5}$$

$$2\mathrm{H}(a) + \mathrm{O}(a) \rightarrow \mathrm{H}_2\mathrm{O}(g) + 3*. \tag{6}$$

Here (g) and (a) mean gas phase and adsorbed species, respectively, and * symbolizes a free adsorption site. Taking into account that steps (5) and (6) are fast and focusing our model on adsorbate-induced phase transition, we assume that H, N, and O coverages are negligible and replace steps (3)–(6) by the following lumped step:

$$\mathrm{NO}(a) + \mathrm{NH}_3(a) \rightarrow \mathrm{H}_2\mathrm{O}(g) + \mathrm{N}_2(g) + 2*. \tag{7}$$

Thus, our model contains only three reaction steps (1), (2), and (7); adsorbate-adsorbate lateral interactions will be neglected in order to reduce the number of parameters in this first approach [19]. The reaction between neighboring NO and NH_3 is closely linked to new experimental evidence [20], which brings further support to the early suggested [21] accelerating effect of coadsorbed oxygen on NH_3 dissociation over Pt(100).

B. Monte Carlo model

In the past there were several efforts toward detailed modeling of reaction systems displaying AIPT using MC simulations. When treating with hex and 1×1 Pt(100) phases, it is a commonly accepted approximation to neglect the existent $\approx20\%$ difference in surface atomic density between them. For instance, Albano (see [18], and references therein) proposed a modified Ziff-Gulari-Barshad (ZGB) model [22] in the dimmer-monomer surface reaction and explored the effect of considering local and global surface reconstruction on reactivity and adsorbate spatial distribution.

Here, we will follow Zhdanov's approach [16,23] to model the AIPT together with the experimental features described in Sec. II A, and apply a lattice gas model that has the following main ingredients:

(i) There are two possible states for every Pt atom, namely, 1×1 or hex. If two nearest neighbors (NN) are in the same state, then interactions are attractive, $-\varepsilon_{MM}$ ($\varepsilon_{MM}>0$); otherwise they are repulsive ε_{MM}.

(ii) We suppose that NO and NH_3 adsorb on on-top sites. Structure-dependent sticking coefficients were introduced as a first approach (S_i^j). The adsorption energy of NO (A) is supposed to increase linearly with the number of NN substrate atoms in the 1×1 state, while NH_3 (B) adsorption is only considered on 1×1 sites and is supposed to have a relatively weak effect on surface reconstruction [9,10]. The parameter associated with the NO-adsorption process is ε_{AM} ($\varepsilon_{AM}>0$), i.e., the change in adsorption energy of NO when the metal atom changes the state from the hex to the 1×1 phase.

(iii) As a first approach, the adsorbate-adsorbate interactions were neglected, as in Ref. [16].

The rules used in our model to simulate the elementary processes are as follows. Nitric oxide or NH_3 is randomly selected with probability p_{NO} and $p_{\mathrm{NH}_3}=1-p_{\mathrm{NO}}$, where p_{NO} and p_{NH_3} are parameters proportional to the partial pressures. The rates for desorption and reaction processes in our simulations are considered to be proportional to the dimensionless parameter p_{des} and to $1-p_{\mathrm{des}}$, respectively. Adsorption on vacant sites is accepted provided the conditions imposed by the sticking coefficients are fulfilled. For ammonia adsorption we supposed $\mathrm{S}_{\mathrm{NH}_3}^{\mathrm{hex}}\approx0$, i.e., it can only take place if the selected vacant site is in the 1×1 state ($S_{\mathrm{NH}_3}^{1\times1}>0$). Nitric oxide has a non-zero sticking coefficient for both surface states, being $1\approx S_{\mathrm{NO}}^{1\times1}>S_{\mathrm{NO}}^{\mathrm{hex}}$ [2].

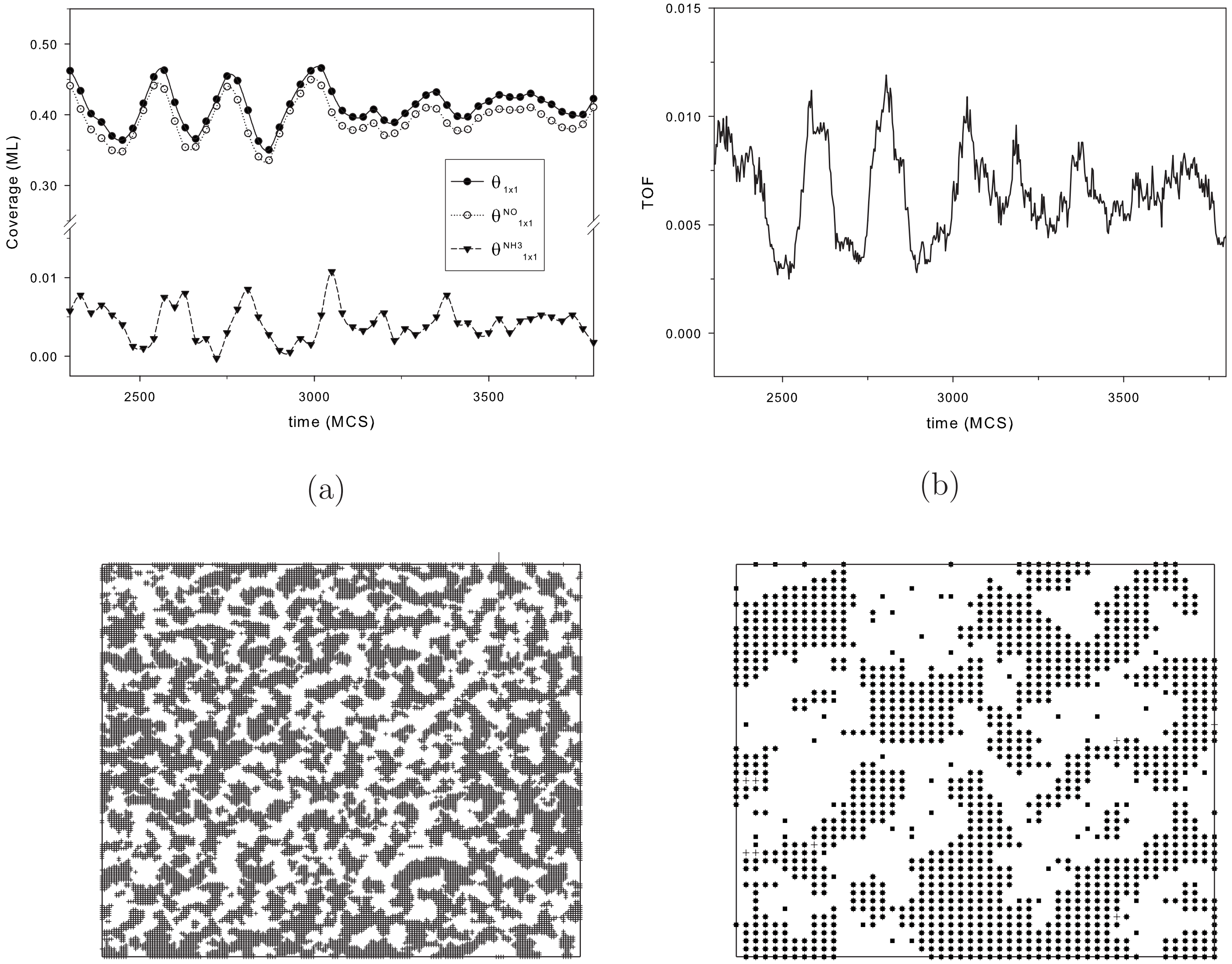
Desorption probability (W_{des}) is affected by the state of the NN surface atoms, i.e., it depends on adsorption energy of the molecule on the surface (i.e., $W_{\mathrm{des}}=\exp(-E_i/k_BT)$, where E_i is a sum of NN adsorbate-surface interactions).

To model diffusion of adsorbed molecules, we also follow Zhdanov [16,23] and we suppose jumps between NN lattice vacant sites. For the jump probability (W_{dif}) we use the Metropolis (MP) rule, $W_{\mathrm{dif}}=1$ if $\Delta E\leq0$, and $W_{\mathrm{dif}}=\exp(-\Delta E/k_BT)$ for $\Delta E>0$, where ΔE is the energy difference between final and initial states of the system.

Reaction occurs whenever NN sites occupied by NO-NH_3 are found, provided the NO site is in the 1×1 state. This reflects the ability of the 1×1 surface structure to dissociate NO and the accelerating effect that oxygen adatoms were proven to have in the NH_3 stripping process. Surface restructuring is also modeled through MP rule-type transitions, i.e., via changes in the states of individual metal atoms and comparison of the initial and final state energies.

III. PARAMETERS

In order to validate our assumptions regarding the model of the reaction system, we introduced realistic values for the



(a) (b)

(c) (d)

FIG. 1. Time evolution for the aperiodic oscillation (AO) regime, $T=400$ K, $p_{NO}/p_{NH_3}=0.5$, and lattice size $L=200$ as discussed in Sec. III. Time evolution for (a) coverages measured in monolayers (ML), and (b) turnover frequency (TOF). Panels (c) and (d) display surface snapshots for $t=3500$ Monte Carlo Steps (MCS). In (c), $L=200$, void places stand for hex sites, and the + symbol represents 1×1 sites. Panel (d) corresponds to a zoomed area of (c) with $L=50$; here we added the ■ symbol to represent adsorbed NO.

energies characterizing the elementary processes. For the energy of the phase transition we used the value of ≈5 kcal per mol of the Pt surface atom, that is, $\Delta E_{PT}=5$ kcal/mol, determined by King *et al.* via calorimetric experiments [24].

We considered the energies for the interactions of CO and NO with the Pt(100) surface structures comparable, as suggested by the work of King *et al.* [10] Consequently, we used the value of ≈12 kcal/mol, measured for the whole energy difference between the adsorption of CO on the hex and 1×1 phases, as a valid approximation when the adsorbate is NO (i.e., $\varepsilon_{AM}=3$ kcal/mol, with $M=$metal, $A=$NO). To account for ammonia adsorption on the 1×1 phase, we used the value ≈3.8 kcal/mol (i.e., $\varepsilon_{BM}=0.95$ kcal/mol, $B=NH_3$), determined by King *et al.* [9]. The simulations were performed using parameter value $p_{des}=0.3$, as in Ref.[23].

We followed Zhdanov [16] and introduced the dimensionless parameters p_{res} and p_{rea} ($p_{res}+p_{rea}\leq1$), characterizing the relative rates of surface restructuring, reaction-adsorption-desorption, and diffusion. The rate of each process is considered to be proportional to p_{res}, p_{rea}, and $1-(p_{res}+p_{rea})$, respectively. The rate of surface restructuring (p_{res}) is known to be lower than that corresponding to reaction processes (p_{rea}), and both of them are much slower than diffusion. We use similar values of these parameters, as in Ref. [16], $N_{dif}=[1-(p_{res}+p_{rea})]/(p_{res}+p_{rea})=990$, with $p_{res}/(p_{res}+p_{rea})=0.3$. Even when these values should change with temperature, the general relationship between rates of surface restructuring, reaction-adsorption, and diffusion processes should hold in a wider range of temperatures [25]. Therefore, in this study we will use as crude approximation the same parameters p_{res} and p_{rea} for the whole range of

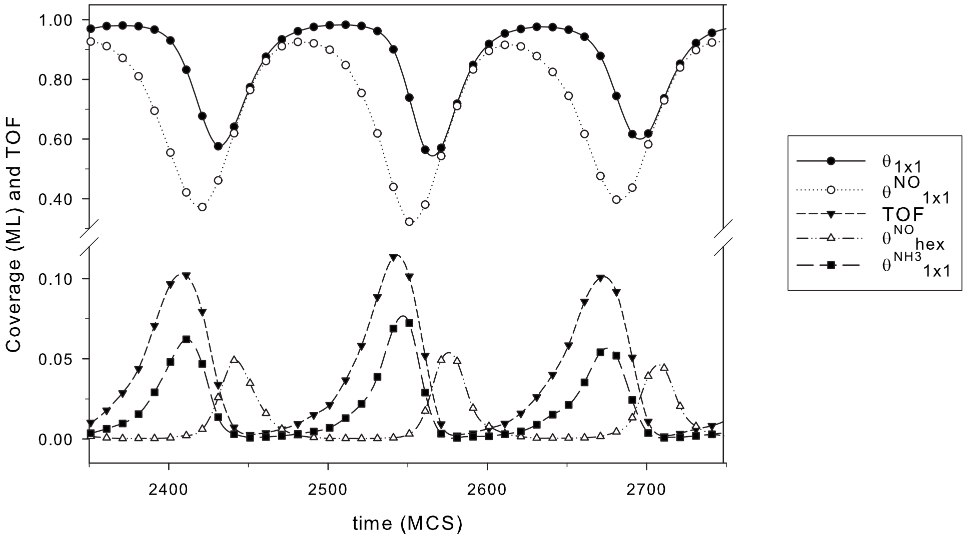


FIG. 2. Segment for roughly two periods in time evolution for the PO regime. Temperature is set to 450 K; other parameters as in Fig. 1.

temperatures studied. For the nonzero sticking probabilities we used constant values $S_{NH_3}^{1\times1}=S_{NO}^{hex}=0.3$.

IV. ALGORITHM

The basic structure of the algorithm used was presented in detail elsewhere by Zhdanov [23]; a brief description of the modifications included will be given here. Reaction, surface restructuring, and diffusion events are tested provided that a randomly generated number $0\leq a_0\leq 1$ fulfils the conditions of being $a_0<p_{rea}$, $p_{rea}\leq a_0<(p_{rea}+p_{res})$, or $a_0\geq(p_{rea}+p_{res})$, respectively.

An *adsorption-reaction-desorption* trial consists of several steps. (1) An adsorption site is randomly selected. (2) Two new random numbers a_1 and a_2 are produced. (3) If the site is an empty 1×1 site, then adsorption of NO(NH_3) is accepted provided that $a_1<p_{NO}$ ($a_1>p_{NO}$) and that $a_2<S_{NO}^{1\times1}$ ($a_2<S_{NH_3}^{1\times1}$). If the site is in the hex state, only NO can adsorb, and the corresponding sticking S_{NO}^{hex} is used. (4) If the site is a 1×1-NO or 1×1-NH_3 site, desorption and reaction trials are performed, respectively, for $a_1\leq p_{des}$ and $a_1>p_{des}$, where p_{des} is the desorption rate parameter described above. For desorption,the process is realized if $a_1\leq W_{des}$, where a_2 is another random number, $W_{des}\leq 1$ is the normalized desorption probability $W_{des}=\exp(-E_i/k_BT)$, and E_i depends on a sum of the NN adsorbate-surface interactions (NO has a higher binding energy on the hex phase than NH_3, the absolute difference is ≈2.1 kcal/mol [9]; this fact was taken into account for the calculation of the corresponding W_{des}). For a successful reaction trial to take place, a randomly selected NN has to fulfill the condition of producing a pair of (NO-1×1)-(NH_3-1×1) sites.

When a *surface restructuring* process is selected, a randomly selected metal atom from the cluster tries to change state according to the MP rule described above. A *diffusion* trial proceeds as follows. Again, a randomly selected site is checked for the presence of adsorbates. (1) If the site is empty, trial ends. (2) If the site is occupied by NO, then one NN is randomly selected. When the site is not empty, trial ends, otherwise the particle has a probability of moving given by the MP rule. (3) If the selected site is occupied by NH_3, then diffusion can only occur provided that the selected NN is an empty 1×1 site. According to the description given in Sec. II B, this setup establishes jumps for ammonia only between 1×1 sites, and for NO a rapid (slow) diffusion process if the initial and final sites are in the hex and 1×1 (1×1 and hex) states, respectively.

Several different initial conditions for the simulations were tested, but given a certain thermalization time, solutions were found to converge. Therefore for the sake of simplicity, in all of our presented simulations we set a clean hex surface as an initial state. We used a square $L\times L$ lattice with $L=200$ and periodical boundary conditions. A reasonable length for Pt-Pt is ≈0.25 nm; then our lattice size $L=200$ represents ≈50 nm. This size was found to be suitable for the intended simulated phenomena. The time measurement commonly used is the Monte Carlo time step (MCS), which involves L^2 trials of any class, so every site is visited once on average during each time unit. Diffusion processes are by far the fastest, so if we use the above-described MCS definition, we would have a time scale primarily connected with diffusion trials. Instead, we used an (adsorption-reaction-desorption)-(surface restructuring)-based time scale. In this way we consider a MCS when L^2 of this subset of trials are performed on average.

V. RESULTS AND DISCUSSION

A. Simulations including AIPT

Simulations showed rich dynamical behavior. As temperature was increased from 370 to 500 K with the pressure parameter ratio fixed to $p_{NO}/p_{NH_3}=0.5$, four different regimes were observed. When the temperature is $T<390$ K, a low-reactive state (P1) appears, in which $\theta_{hex}\approx1$ and NH_3 (unlike NO) is unable to adsorb. No reaction (quantified via the turnover frequency, TOF=number of reaction events per unit time per site) was observed, and a low θ_{NO}^{hex} characterized the steady state. The last stage in temperature evolution starts when $T>480$ K, and also shows a low-reactive state (P2),

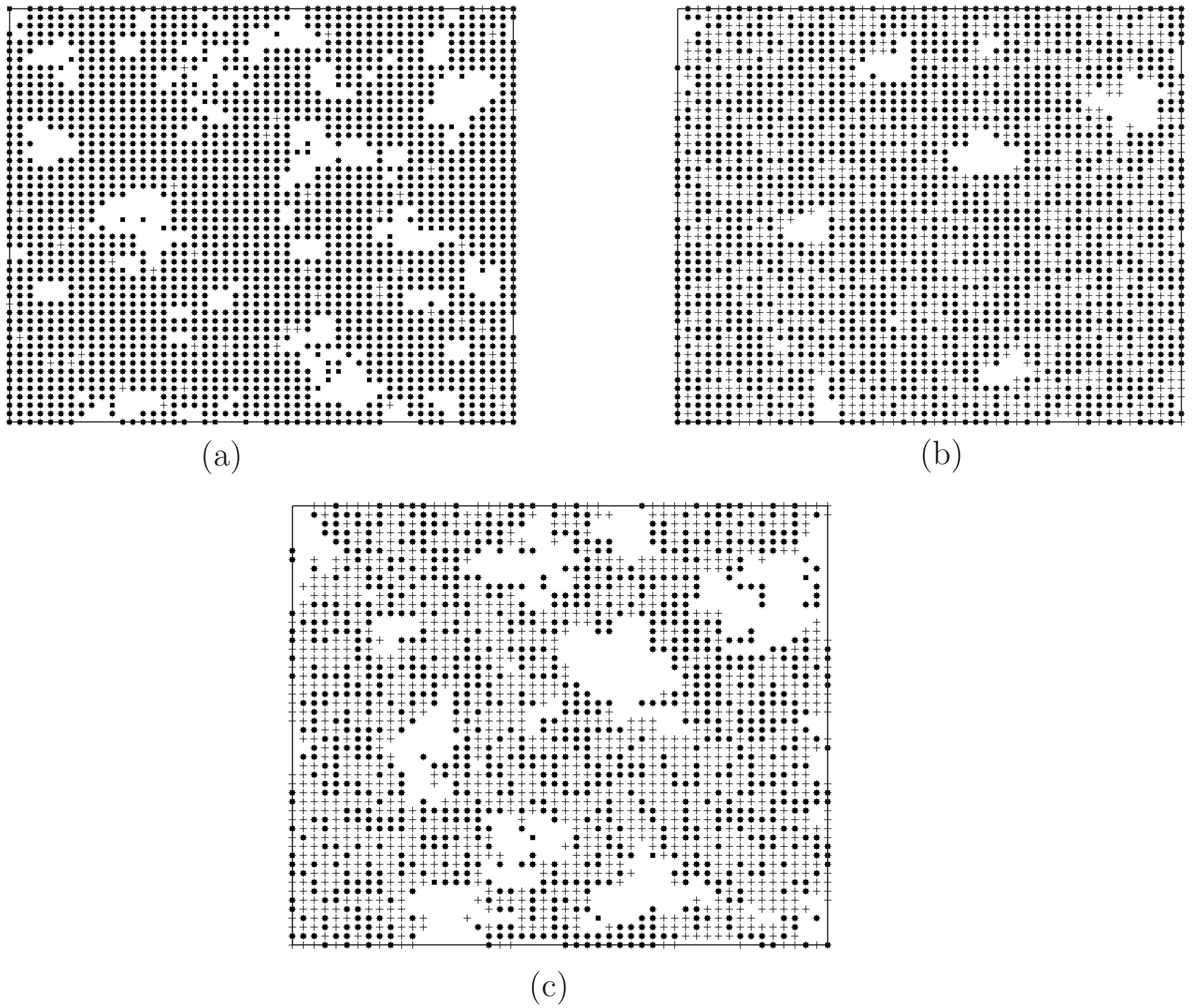


FIG. 3. Surface evolution of reaction system with AIPT in the PO regime for minimum, intermediate, and maximum TOF; all parameters set as in Fig. 2. Panels (a), (b), and (c) display enlarged areas with $L=50$ of the lattice with + and void symbols representing 1×1 and hex phases. Sites occupied with NO are also displayed symbolized with ■.

where TOF falls again to zero. The inactive P2 state is a predominant $NO-1\times1$ covered surface.

In between these two low-reactive states we observed interesting dynamical behavior. Figure 1 illustrates the regime obtained when $390\text{ K}<T<410\text{ K}$. Aperiodic oscillations (AO) with nonzero TOF characterize this parameter region. It can be observed in Fig. 1 that the reason for the low TOF value is the low coverage of ammonia ($\theta_{NH_3}^{1\times1}$) on the surface. Snapshots of the surface show the appearance of sharp-boundary 1×1 islands (mean diameter $\approx5-10$ nm) almost fully NO covered.

If temperature is further increased and the value is maintained between 410 and 480 K, periodic oscillations (PO) appear. In Fig. 2 oscillations in reactant coverages and TOF with constant period and amplitude can be observed. A rationalization similar to that proposed by Imbihl *et al.* [2] and reproduced theoretically using the LFI mechanism [13] can be used to explain the catalytic cycle obtained.

Starting from the minimum in a 1×1 phase a decrease of NO coverage in the hex phase (θ_{NO}^{hex}), and an increase in $\theta_{NO}^{1\times1}$ can be observed. This indicates the onset of the AIPT. On the 1×1 phase, NO can adsorb and react with NH_3; this can be seen in the steep increase in ammonia coverage $\theta_{NH_3}^{1\times1}$ coincident with the TOF peak. With the 1×1 phase being no longer stabilized by NO, which has been reacted away (low $\theta_{NO}^{1\times1}$), the surface reconstructs back into the initial state and the cycle starts again.

In Fig. 3 we present the surface spatial structure at three different stages of a period in time evolution from Fig. 2, namely, minimum, intermediate, and maximum TOF value ($t=2450,2525,2550$ MCS). Here the difference between NO coverage at maximum and minimum is evident, the snapshot at $t=2550$ MCS allows us to observe how vacant sites in the newly 1×1 phase formed appear, and a reaction can now take place.

B. Simulations without AIPT

In this section we consider a modified version of our model that excludes the occurrence of the AIPT. In this way, within the reach of our simplified model, we test an alternative hypothesis for the occurrence of kinetic oscillations.

We introduced the following changes to the model presented in Sec. II B. The entire surface was supposed to be permanently in a "pseudo-1×1" state, where both ammonia and NO can adsorb and react. Sticking coefficients and all remaining parameters were maintained as in Sec. III. Since every site is now equivalent, diffusion becomes a nonactivated process for all the adsorbates.

The dynamical behavior obtained was significantly different; two low-reactive states were found in the limits of the studied temperature range (for the $T<420$ K-NH_3 covered surface, and for $T>540$ K-NO covered surface); but no transition whatsoever into oscillating regimes resembling AO or PO was observed. For temperatures inside the range 420 K $<T<540$ K, the system showed nonzero NO and NH_3 coverages, and TOF. No organized spatial structures such as islands, or oscillations (both periodic and aperiodic) in time evolution of coverages or TOF were observed on the lattice during simulations using this modified model.

VI. CONCLUSIONS AND OUTLOOK

In this work we have proposed a model to describe some of the processes involved in the catalytic reduction of NO with NH_3 on a Pt(100) single crystal surface. The model considers an adsorbate-induced phase transition (AIPT) between two surface structures (the reconstructed inactive hex and the active 1×1 phases), each one of them having different properties regarding the interaction with adsorbates.

The model incorporates temperature dependence through Arrhenius type relationships in activation energies for all the elementary processes. In spite of its simplicity (e.g., we do not consider adsorbate-adsorbate interactions, nor sticking coefficient temperature dependence among other approximations), the model is capable of reproducing the complicated dynamical behavior displayed by the reaction system. As the temperature is varied in the range of $\approx 400-500$ K, periodic oscillations (PO), aperiodic oscillations (AO), and two low-reactive regimes (P1) and (P2) are established. The simulation output closely relates to the known experimental behavior [2], in the sense that increasing temperature leads to a transition from nonsynchronized to synchronized response (i.e., transition from aperiodic to periodic oscillations).

By carrying out simulations, including AIPT, we have identified, within the limits of our simplified model, its importance in the onset of kinetic oscillations on our reaction system. These observations are in line with recent experimental work by McMillan *et al.* [26], who studied ammonia oxidation with NO on polycrystalline platinum and confirmed the key role of the AIPT occurring in the (100) face for the appearance of oscillations.

Regarding the spatial scale utilized in these simulations and the present characterization of the reaction system phase diagram, it seems promising future work oriented toward the elucidation of the effect of surface defects on the lattice already started using mean field reaction-diffusion simulations [13].

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