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Perturbation of period-2 oscillations in catalytic reactions accompanied by surface restructuring

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We present Monte Carlo simulations illustrating the effect of periodic forcing on period-2 oscillations related to the interplay of catalytic reaction and surface restructuring. The oscillations are found to be fairly stable if the external frequency equals the main internal frequency. In contrast, perturbations with other frequencies may easily change the type of oscillation. In particular, perturbations with double frequency convert period-2 oscillations into period-1 oscillations with the imposed frequency.

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I. INTRODUCTION

Periodic forcing of reaction kinetics via, e.g., variation of reactant pressure(s) or temperature is one of the useful tools employed in basic and applied studies in chemistry in general and in heterogeneous catalysis in particular [1]. In experiments focused on the complex behavior of catalytic reactions, this strategy is widely used to stabilize period-1 oscillations (this is easily possible if the external and internal frequencies are equal) or to generate quasiperiodic or irregular oscillations. In applied catalysis, periodic forcing provides additional opportunities for optimization of the reactor performance [2]. In a more general context, periodic perturbations can be used to control chaos [3] and induce complex spatiotemporal behavior [4]. Despite all these advances and/or applications, many interesting aspects of periodic forcing of chemical reactions are still open for investigation. In particular, it is not clear how periodic perturbations may influence period-2 oscillations. Our Monte Carlo (MC) simulations of catalytic oscillations clarify this point.

Oscillations in heterogeneous catalytic reactions often result from the interplay of rapid reaction steps and a relatively slow ‘‘side’’ process, such, as e.g., adsorbate-induced surface restructuring, oxide formation, or carbon deposition (see the recent reviews [5,6]). Physically, this means that oscillations are frequently accompanied by phase separation on the mesoscopic scale. Under such circumstances, simple mean-field (MF) models based on the conventional mass-action law are strictly speaking not applicable. One should rather use sophisticated MF kinetic equations or the MC technique. In our MC simulations, we employ a generic model which was proposed [7] to describe surface-restructuring-related oscillations, period doubling, and irregularities in the kinetics of NO reduction by H_2 on Pt(100) (for a review of the corresponding experimental and theoretical studies, see Sec. 6 in Ref. [6]). The key factors lying behind oscillations in this reaction are similar to those in other reactions with participation of NO on Pt(100). Thus, the domain of applicability of our main conclusions is expected to be broad. To extend the understanding of the problem under consideration, we will also briefly comment on more conventional MF kinetic models predicting period-2 oscillations.

II. MODEL

The mechanism of the NO-H_2 reaction on Pt(100) includes (i) NO adsorption, desorption, and decomposition, (ii) reversible dissociative adsorption of H_2, (iii) nitrogen desorption, and (iv) reactions between adsorbed H, O, N, and NO resulting in the formation and desorption of H_2O, NH_3, and N_2O. At the most interesting temperatures (above 430 K), steps (ii)–(iv) are rapid and the surface coverage by H, O, and N is low. This makes it possible to use a reduced reaction scheme, involving explicitly only reversible NO adsorption and decomposition. The other reaction steps are taken into account implicitly by removing the NO-decomposition products (N and O) from the surface immediately after decomposition events. Thus, we have only one adsorbed species, NO, which is able to induce changes in the surface structure.

To mimic the NO-induced restructuring of the Pt(100) surface [specifically, the transition from the quasihexagonal (‘‘hex’’) arrangement of Pt atoms, which is stable before NO adsorption, to the (1×1) arrangement stable after NO adsorption], we use the lattice-gas model.

(1) Metal atoms M ($M\equiv$Pt) form a square lattice. Every M atom may be in a stable or metastable state (the terms ‘‘stable’’ and ‘‘metastable’’ refer to states that are stable and metastable on the *clean* surface, and accordingly the corresponding phases mimic the ‘‘hex’’ and (1×1) phases, respectively). The energy difference of these states is ΔE. The nearest-neighbor (NN) lateral M-M interaction is considered to be attractive, $-\epsilon_{MM}$ ($\epsilon_{MM}>0$), if the atoms are in the same states, and repulsive, ϵ_{MM}, if the states are different. The next-nearest-neighbor (NNN) interactions are ignored. (Note that the M-M interactions introduced actually describe the deviation from the average value. For this reason, the sign of the M-M interactions may be either positive or negative depending on the arrangement of metal atoms.)

(2) Adsorbed particles A ($A\equiv$NO) occupy hollow sites (this assumption is not essential, because for adsorption on top sites the structure of the formal equations is the same). The adsorption energy of a given particle is considered to increase linearly with the number of NN substrate atoms in the metastable state (this is a driving force for the phase transition). In particular, the increase of the adsorption energy of an A particle after the transition of one NN substrate atom from the stable to the metastable state is ϵ_{AM} ($\epsilon_{AM}>0$). The adsorbate-adsorbate lateral interactions are ignored for simplicity.

The adsorbate-substrate Hamiltonian corresponding to the

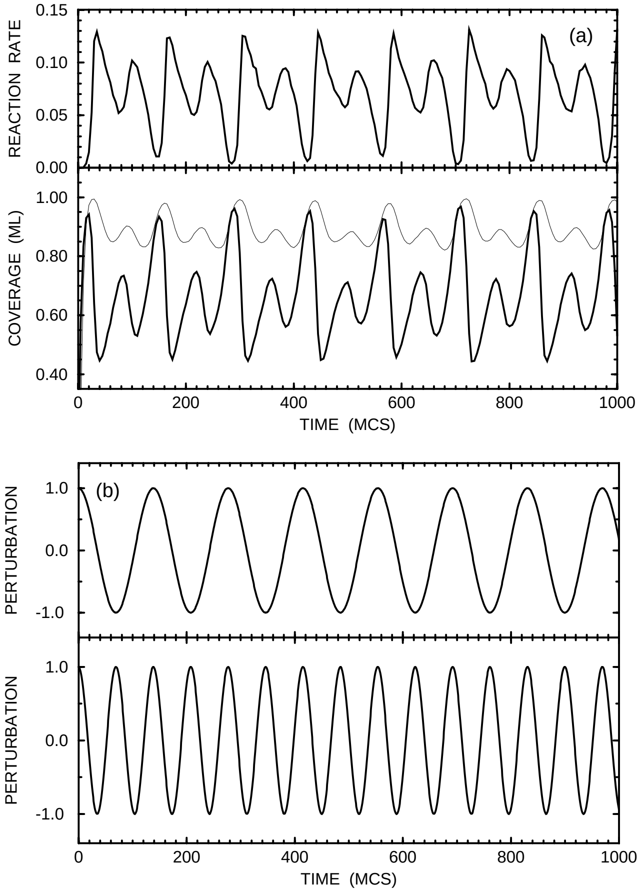


FIG. 1. (a) NO decomposition rate (per site per MCS), NO coverage (ML≡monolayer), and fraction of Pt atoms in the state representing the (1×1) phase (thick and thin lines, respectively) in the case of unperturbed period-2 oscillations with $p_{\mathrm{NO}}=0.3$. (b) Harmonics with the main and double frequencies (upper and lower panels) used for perturbation.

assumptions above contains the M-M and A-M interactions

$$H=H_s+H_{as},$$

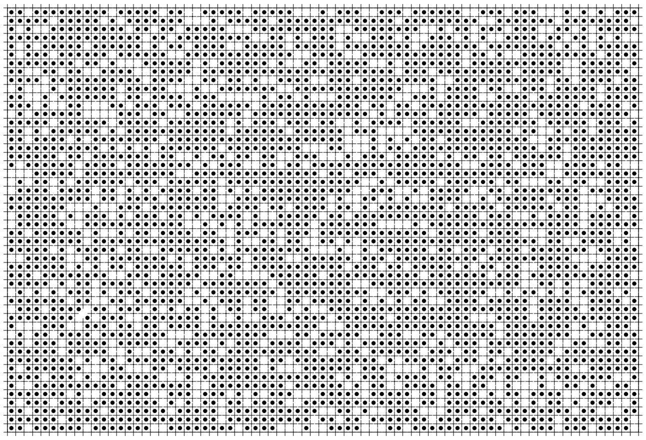
$$H_s=\Delta E\sum_i n_i^M-4\epsilon_{MM}\sum_{i,j}(n_i^M-1/2)(n_j^M-1/2),$$

$$H_{as}=-\sum_{i,j}\epsilon_{AM}n_j^An_i^M,$$

where n_i^M is the variable characterizing the state of atom i ($n_i^M=1$ or 0 is assigned to the metastable and stable states, respectively), n_i^A is the occupation number of the adsorption sites, and Σ_{ij} means summation over nn pairs. Mathematically, the lattice-gas model defined by these equations is equivalent to a model consisting of two subsystems of Ising spins. It predicts an adsorbate-induced first-order phase transition provided that the adsorbate-substrate interaction is sufficiently strong.

The procedure for introducing the rate constants for all the relevant elementary rate processes in accordance with the model outlined was described in detail earlier [7]. Here, we recall only that the decomposition of A (i.e., of NO) is considered to occur provided that (i) at least one NN site is vacant and (ii) all the M atoms adjacent to A and to a vacant site are in the metastable state. The latter condition takes into account that NO decomposition occurs primarily on the (1×1) phase. To simulate the reaction kinetics, we use the set of parameters [7] $\Delta E/k_{\mathrm{B}}T=2$, $\epsilon_{MM}/k_{\mathrm{B}}T=0.5$, and $\epsilon_{AM}/k_{\mathrm{B}}T=2$, corresponding to fixed temperature $T\simeq0.40T_c$ (T_c is the critical temperature). These parameter values were chosen on the basis of available experimental data (see the discussion in Refs. [6,7]).

(a) t=720 MCS



(b) t=820 MCS

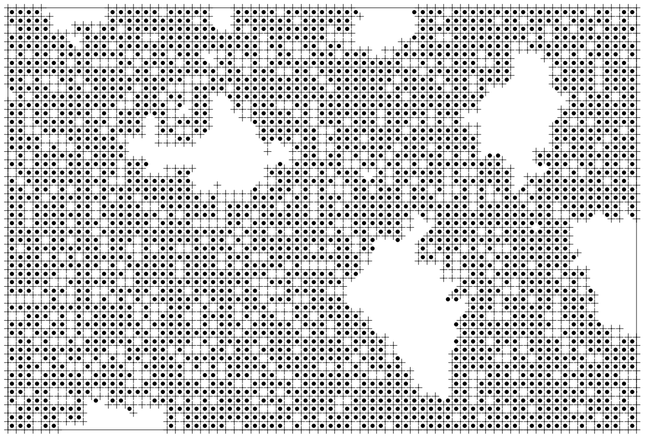


FIG. 2. Typical snapshots of a (75×50) fragment of the (200×200) lattice for the MC run, shown in Fig. 1(a), at the moments when the fraction of Pt atoms in the state representing the (1×1) phase is (a) maximum and (b) minimum. Filled circles and plus signs exhibit, respectively, adsorbed particles and substrate atoms forming the (1×1) phase. Metal atoms on the areas mimicking the "hex" phase are not shown.

Surface restructuring, adsorption-reaction steps, and diffusion of A particles are simulated with probabilities p_{res}, p_{rea} ($p_{\mathrm{res}}+p_{\mathrm{rea}}\leqslant1$), and $1-p_{\mathrm{res}}-p_{\mathrm{rea}}$, respectively. In reality, surface restructuring is slower than the adsorption-reaction steps (i.e., $p_{\mathrm{res}}<p_{\mathrm{rea}}$), which are in turn much slower compared to A diffusion (i.e., $p_{\mathrm{res}}+p_{\mathrm{rea}}\ll1$). In our simulations, we employ $p_{\mathrm{res}}/(p_{\mathrm{res}}+p_{\mathrm{rea}})=0.3$. In the framework of this scheme, the ratio of the rates of A diffusion and

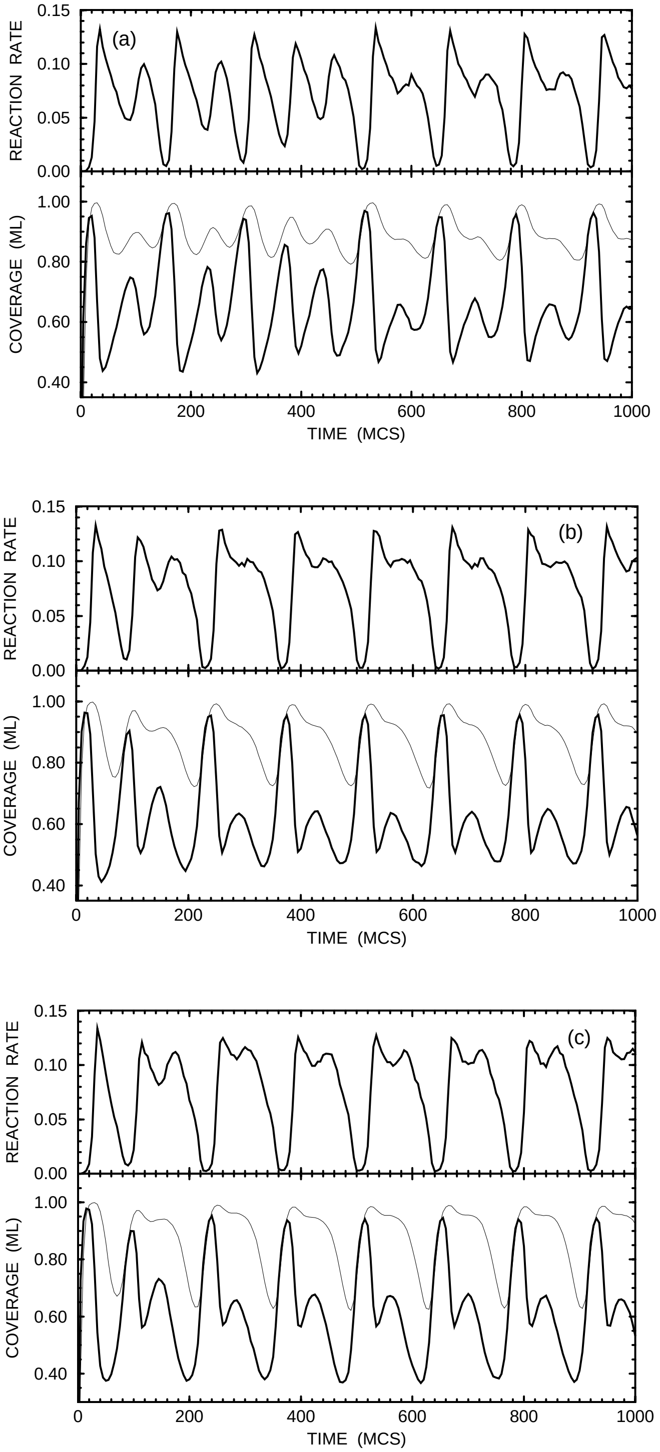


FIG. 3. Forced oscillations for $\chi=0.1$ (a), 0.3 (b), and 0.5 (c) in the case when the external and internal frequencies are equal. The designations are as in Fig. 1(a).

the other processes is $N_{\mathrm{dif}}\equiv(1-p_{\mathrm{res}}-p_{\mathrm{rea}})/(p_{\mathrm{res}}+p_{\mathrm{rea}})$. The results are presented for $N_{\mathrm{dif}}=1000$.

Inside the catalytic cycle, A adsorption on vacant sites is performed with probability p_{NO} (p_{NO} is the governing parameter). A desorption and decomposition are simulated with probabilities p_{des} and $1-p_{\mathrm{des}}$, respectively. More specifically, the rate of A desorption depends on the A-M lateral interactions [7]; the parameter p_{des} corresponds to the maximum desorption rate. The simulations are executed for $p_{\mathrm{des}}=0.2$ (note that this value is somewhat lower than that used in Ref. [7]).

Perturbation of the reaction kinetics is assumed to occur via periodic modulation of the NO pressure. This means that the parameter p_{NO} depends on time as

$$p_{\mathrm{NO}}=p_{\mathrm{NO}}^{0}[1+\chi\cos(\omega_{\mathrm{ex}}t)],$$

where p_{NO}^{0} is the average value, χ the modulation amplitude, and ω_{ex} the external frequency.

Initially (at $t=0$), the surface was considered to be clean and all the M atoms to be in the stable state. The results were obtained for an $(L\times L)$ M lattice with $L=200$ and periodic boundary conditions. To measure time, we employ the so-called MC step (MCS) defined as $(L\times L)$ attempts of the adsorption-reaction-surface-restructuring events. The algorithm of our present simulations is identical to that employed earlier [7].

III. RESULTS OF SIMULATIONS

With the specifications above, the model predicts well-developed period-2 oscillations for $\chi=0$ at $p_{\mathrm{NO}}\simeq0.3$ [Fig. 1(a)]. The oscillations are established just after the beginning of MC runs (in fact the transient period is absent). During oscillations, the islands representing the ‘‘hex’’ phase grow and shrink (Fig. 2). The island size is relatively small, because the adsorbed overlayer is close to saturation. (For period-1 oscillations, the island size is larger [7].)

To force the oscillatory kinetics shown in Fig. 1(a), we used perturbations with various frequencies. The most interesting results were obtained for the frequency, $\omega_{\mathrm{ex}}=0.0454\ \mathrm{MCS}^{-1}$, equal to the main internal frequency, and also for the double frequency $\omega_{\mathrm{ex}}=0.0908\ \mathrm{MCS}^{-1}$ [Fig. 1(b)].

The perturbations with the main frequency are found to result in kinetic irregularities but only in the beginning (Fig. 3). The duration of the transient period slightly decreases with increasing modulation amplitude. For the runs with $\chi=0.1$, 0.3, and 0.5, for example, the duration of the transient period is, respectively, about 500, 200, and 200 MCS. During this period, the internal dynamics and external perturbation adjust to each other. With increasing time, the system relaxes and exhibits well-developed period-2 oscillations. The shape of the established period-2 oscillations depends on the modulation amplitude. It is of interest that such oscillations are observed even for the perturbation with the maximum amplitude, i.e., for $\chi=1.0$ (not shown).

In contrast, the perturbations with the double frequency leave unchanged the type of oscillations [Fig. 4(a)] only if the modulation amplitude is small (smaller or about 0.05). With increasing modulation amplitude, the period-2 oscillations are easily converted into period-1 oscillations with the imposed frequency [Figs. 4(b) and 4(c)]. The transient period in these cases is typically shorter, or about 200 MCS.

Detailed qualitative explanation of period-2 oscillations is usually far from straightforward. Nevertheless, careful in-

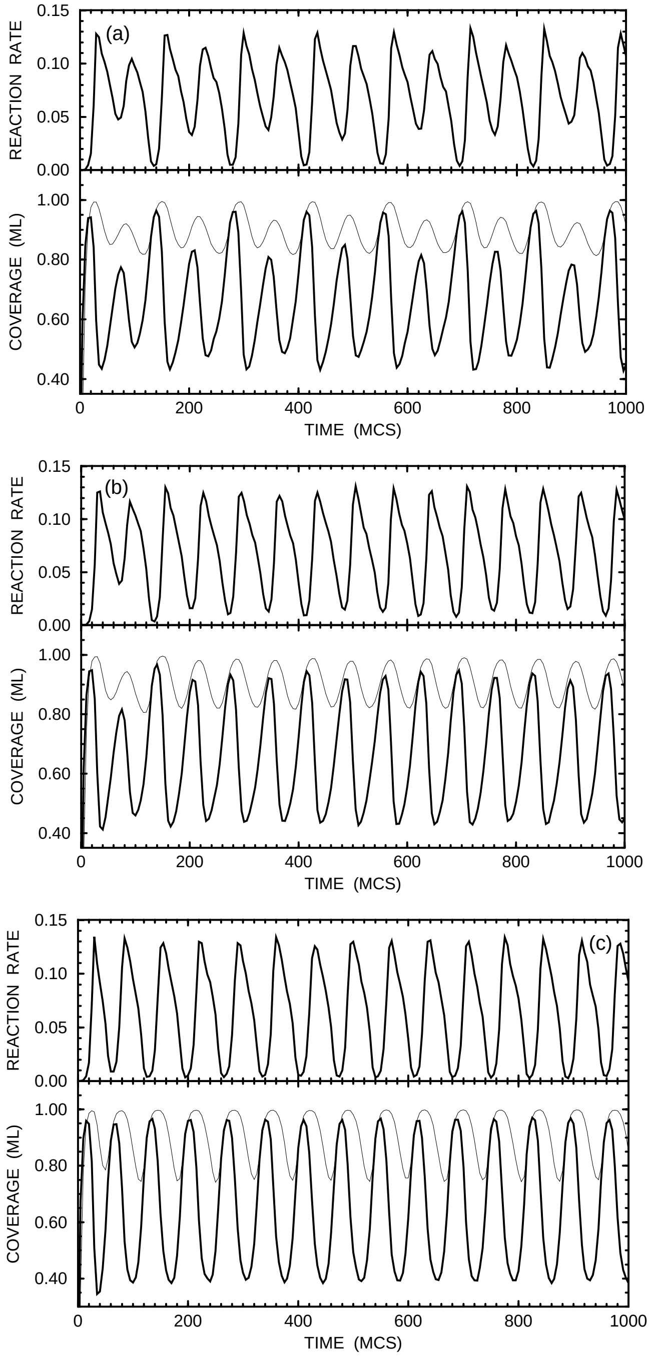


FIG. 4. Forced oscillations in the case of perturbations with the double frequency and $\chi = 0.05$ (a), 0.1 (b), and 0.3 (c). The designations are as in Fig. 1(a).

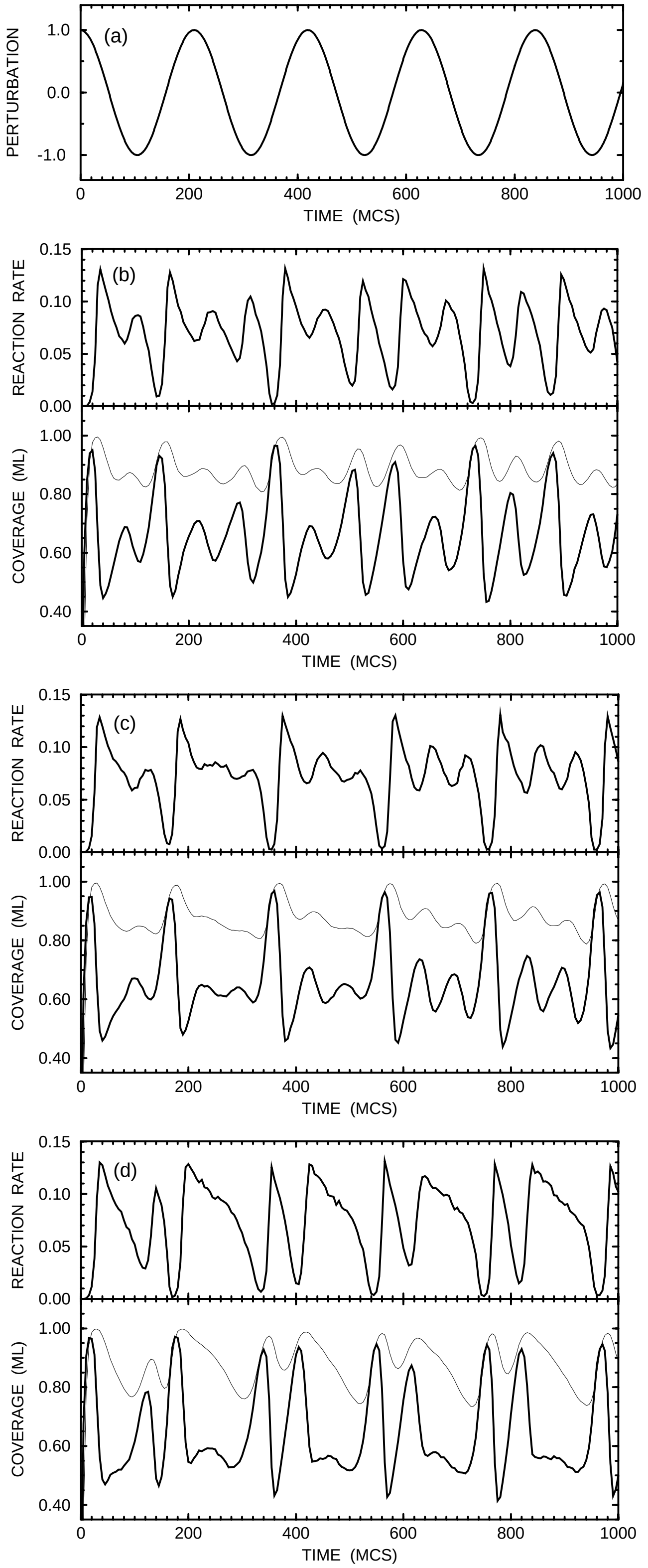


FIG. 5. Perturbation harmonic (a) and reaction kinetics for $\omega_{\mathrm{ex}} = 0.03$ and $\chi = 0.05$ (b), 0.1 (c), and 0.3 (d). The designations are as in Fig. 1(a).

spection of the results obtained makes it possible to rationalize what we have here. In particular, the snapshots shown in Fig. 2 indicate that at the moments when the adsorbate coverage is maximum the metal atoms are almost entirely in the (1×1) state. With decreasing coverage, this phase shrinks and one can observe islands of the other phase [Fig. 2(b)]. The growth of these islands occurs even near the points where the adsorbate coverage reaches maxima located between the main maxima. Thus, basically, the period-2 oscillations appear due to the interplay of the conventional steps (adsorption, desorption, and decomposition) and the initial stages of island growth. The perturbations with the main internal frequency increase coverage near the main maxima and decrease coverage near the intermediate maxima. Both

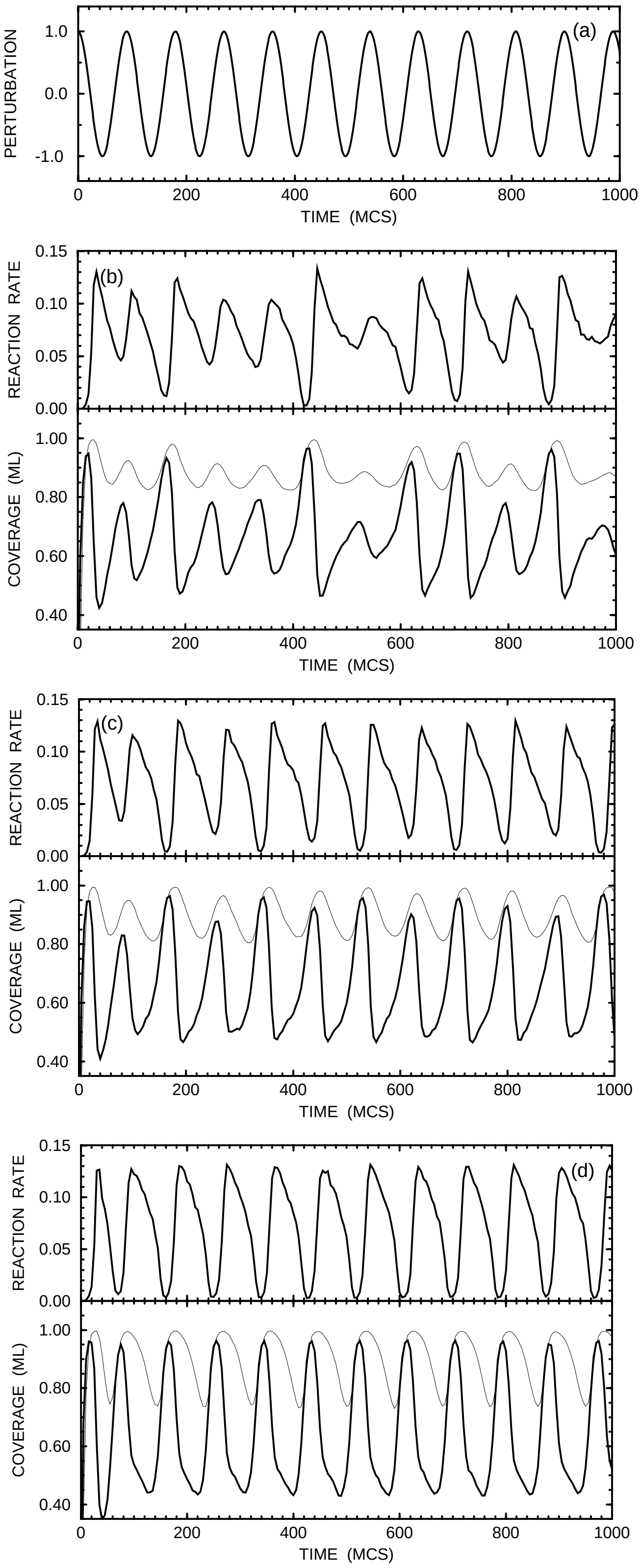


FIG. 6. As Fig. 5 for $\omega_{ex} = 0.07$.

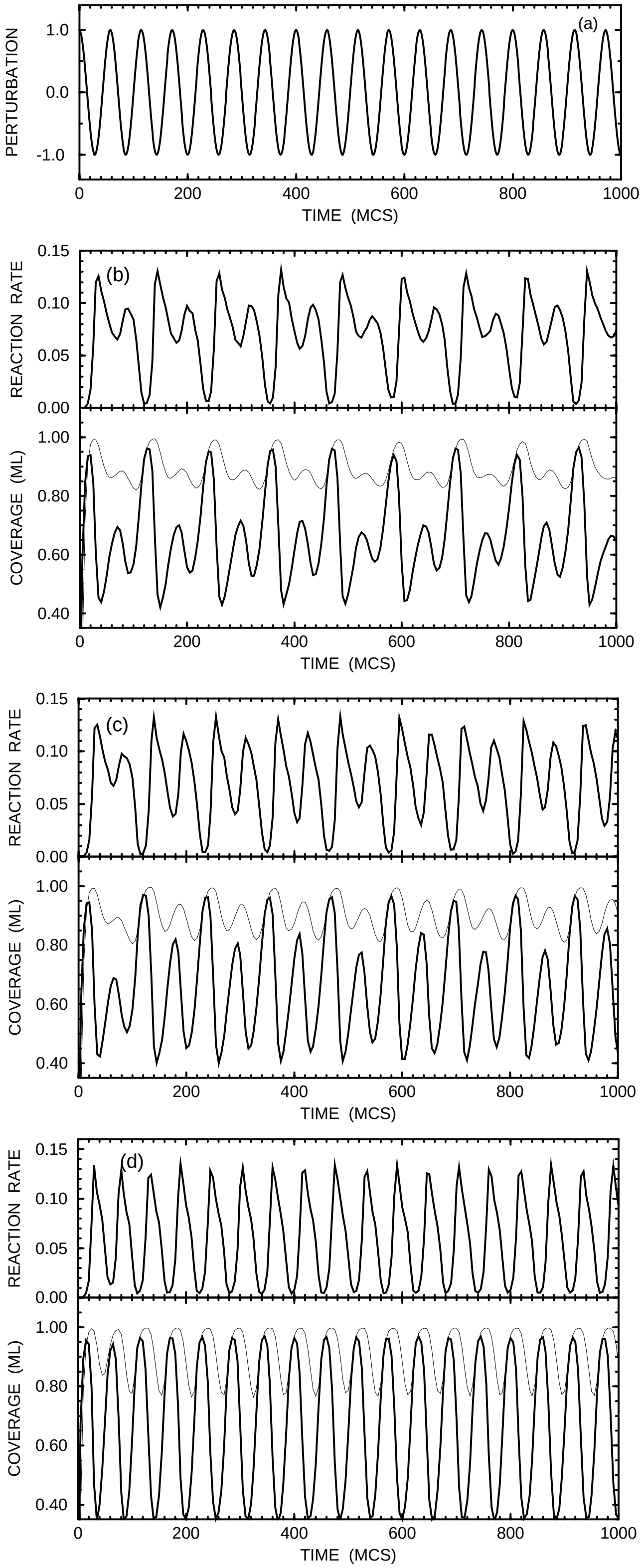


FIG. 7. As Fig. 5 for $\omega_{ex} = 0.11$.

these changes act in line with the factors resulting in the period-2 oscillations (in particular, the decrease of coverage near the intermediate maxima facilitates island growth at these stages). For this reason, the period-2 oscillations are remarkably stable with respect to the perturbations with the main internal frequency. In contrast, the perturbations with the double frequency increase coverage near the main maxima and also near the intermediate maxima. The latter slows down the island growth near the intermediate maxima and accordingly stimulates conversion of the period-2 oscillations into period-1 oscillations with the imposed frequency.

The analysis of perturbations of period-2 oscillations at the main and double frequencies was the primary goal of our simulations. To extend the presentation, we have however also studied the model behavior at three other external frequencies $\omega_{ex}=0.03$, 0.07, and 0.11, which are lower than the main frequency, between the main frequency and the double frequency, and above the double frequency, respectively.

For $\omega_{ex}=0.03$, the oscillations are first irregular [Fig. 5(b) for $\chi=0.05$] and then converted to period-3 oscillations with the imposed frequency [Figs. 5(c) and 5(d) for $\chi=0.1$ and 0.3].

For $\omega_{ex}=0.07$, the oscillations are first irregular [Fig. 6(b) for $\chi=0.05$] and then converted to period-2 oscillations with a frequency equal to one-half the forcing frequency [Fig. 6(c) for $\chi=0.1$] and eventually to period-1 oscillations with the forcing frequency [Fig. 6(d) for $\chi=0.1$ and 0.3].

For $\omega_{ex}=0.11$, the oscillations are easily converted to period-2 oscillations with a frequency equal to one-half the forcing frequency [Figs. 7(b) and 7(c) for $\chi=0.05$ and 0.1] and then to period-1 oscillations with the forcing frequency [Fig. 6(d) for $\chi=0.1$ and 0.3].

IV. CONCLUSION

In summary, our MC simulations indicate that period-2 oscillations in catalytic reactions accompanied by surface restructuring may be fairly stable with respect to perturbations with a frequency equal to the main internal frequency. Perturbations with other frequencies may easily change the type of oscillation. In particular, perturbations with double frequency convert period-2 oscillations to period-1 oscillations.

Finally, it is appropriate to note that the period-1 and -2 oscillations predicted by our MC model are fairly robust in the sense that the corresponding areas of the governing parameter(s) are relatively broad. More conventional MF models including only chemical steps (adsorption, desorption, and elementary reactions) often predict much narrower oscillatory windows. In such cases, the periodic perturbations may shift the system to areas that are far from the period-1 and/or -2 domains even if the perturbation amplitude is relatively small. Under such circumstances, the perturbations may easily destroy period-2 oscillations even if the imposed frequency equals the main internal frequency (we have proved this prediction by using a MF model proposed [8] for describing oscillations in H_2 oxidation on Pt).

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