

Global Synchronization via Homogeneous Nucleation in Oscillating Surface Reactions

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(Received 22 April 1999)

The mechanism leading to globally synchronized oscillations in the $\text{CO} + \text{O}_2/\text{Pt}(110)$ reaction system is investigated by means of Monte Carlo simulations. The model considers the reconstruction of the surface via phase border propagation and spontaneous phase nucleation. The reason for global oscillations turns out to be the spontaneous phase nucleation. This nucleation, which is modeled as a weak noise process, results in a random creation of dynamic defects and leads to global synchronization via stochastic resonance. The mechanism of global coupling via the gas phase, as it is proposed to date, does not occur.

PACS numbers: 82.65.Jv, 05.45.Xt, 82.20.Mj, 82.20.Wt

Kinetic oscillations in heterogeneous catalytic surface reactions on single crystal surfaces occur in many reaction systems, e.g., $\text{CO} + \text{O}_2/\text{Pt}(100)$ [1], $\text{CO} + \text{O}_2/\text{Pt}(110)$ [2], and $\text{CO} + \text{NO}/\text{Pt}(100)$ [3,4]. For a detailed review see Ref. [5]. A very rich and interesting system is the $\text{CO} + \text{O}_2$ reaction on Pt(100) and Pt(110) under UHV conditions. On Pt(100) local, irregular oscillations occur in a wide parameter interval, whereas on Pt(110) globally synchronized oscillations exist only in a very narrow parameter interval. Both surfaces exhibit an $\alpha \rightleftharpoons \beta$ surface reconstruction, where α denotes the *hex* or 1×2 phase on Pt(100) or Pt(110), respectively. β denotes the unreconstructed 1×1 phase in both cases. Both surfaces have qualitatively quite similar properties with the exception of the dissociative adsorption of O_2 . The ratio of the sticking coefficients of O_2 on the two phases is $s_\alpha:s_\beta \approx 0.5:1$ for Pt(110) and $s_\alpha:s_\beta \approx 10^{-2}:1$ for Pt(100) [5]. As has been shown in experiment [5] and in Monte Carlo (MC) simulations this difference results in completely different spatiotemporal pattern formation of the surface phases [6,7]. From the calculations one derives that on Pt(100) small mesoscopic islands of the β phase form in a macroscopic α phase. Reactions on these phase islands are locally synchronized via CO diffusion. On Pt(110) the system oscillates between α islands in a macroscopic β phase (structure S1) and β islands in a macroscopic α phase (S3). The system shows a transition state where both phases exist only as mesoscopic islands (S2) [7]. In this case the synchronization is much more effective, but remains local in comparison to real catalyst surfaces.

Experiments show that on Pt(110) periodic variations in the partial pressure of CO, $\delta p_{\text{CO}}(t)$, occur during the reaction [8]. It is assumed that these originate from local oscillations. Because the mean free path is very large in the gas phase global variations are assumed to develop which in turn synchronize the oscillations on the surface. This scenario is similar to the case of an external periodic variation of p_{CO} or p_{O_2} [9] only that now the system is assumed to autonomously develop such a self-synchronized

periodic force which leads to resonance effects. This global coupling (GC) has been extensively investigated via mathematical modeling [10–12]. But here a critique is necessary. Mean field type models neglect all correlations and do not contain any length scales whatsoever. But the latter ones, in particular, should be exceedingly important. In addition artificial nonlinearities and many parameters taken from experiment are commonly used in these models. Therefore the origin of the globally synchronized oscillations necessarily remains unclear.

In this Letter we question the idea of the GC process and propose stochastic resonance (SR) [13] as the origin of cooperative effects. Of course we do not question the experimental results where the existence of autonomous variations in p_{CO} [8] was found or where synchronized oscillations have been observed on two disconnected Pd crystals [14]. But there are two possibilities to explain the experimental observations: (i) local reactions initiate a global periodic variation in p_{CO} which synchronizes the oscillations (i.e., GC) or (ii) globally synchronized oscillations originating from another process lead to periodic variations in p_{CO} . We intend to switch the role of what is the cause and what is the consequence compared to the prevailing thought.

(i) From dimensional considerations it follows that the coupling strength between the gas phase and the surface reaction is given by L^2/V_{reac} , i.e., $\delta p_{\text{CO}}(t) \propto V_{\text{reac}}^{-1}$, where V_{reac} is the volume of the reactor and L the side length of the catalyst. For large volumes this coupling strength can be neglected because thermal fluctuations of the pressure as an intensive variable in statistical thermodynamics have a different dependence on the volume, $\delta p_{\text{therm}} \propto V_{\text{reac}}^{-1/2}$, and $\delta p_{\text{CO}}(t) \ll \delta p_{\text{therm}}$ holds for large V_{reac} . Therefore the suggested coupling mechanism via GC is invalid. There also exists an experimental hint that GC is not the reason for synchronized oscillations on Pt(110). In a study of forced oscillations [9] an external periodic modulation of the partial pressures is applied. As a consequence the GC via the gas phase should

also be strongly disturbed or even removed. In this study sub- and superharmonic frequency entrainment and resonance phenomena occur quite in general; thus there has to be an internal synchronization mechanism which leads to these resonance phenomena with the externally varied partial pressures and which is not mediated via the gas phase.

(ii) The surface reaction systems considered here are dominated by fast CO diffusion at the ambient reaction temperature. Adsorbed O atoms can be taken as immobile. Diffusion systems exhibit a so-called diffusion length $l = \sqrt{Dt}$, where D denotes the diffusion constant. During an oscillation period T the CO molecules can react with adsorbed O atoms and initiate the lifting of the reconstruction of the surface, which depends on CO, in a domain of size $\xi = \sqrt{DT}$. ξ is the synchronization length and all processes within this domain are synchronized via CO diffusion. A very strong diffusion would lead to global synchronization ($\xi \gg L$), but for real single crystal surfaces $\xi \ll L \approx 100 \mu\text{m}$ holds for reasonable values of D . Furthermore, the difference in the CO diffusion constants on Pt(100) and Pt(110) is too small to explain the occurrence of local oscillations in the former case and of global oscillations in the latter case. If the synchronization is mainly based on diffusion processes, there must be a strong amplification in the case of the Pt(110) surface. We will show that this amplification is a result of spontaneous nucleation of dynamic defects, which is modeled as a noise process and leads to global synchronization via SR.

We propose a very simple model which contains the essential physics. This model has only a few free parameters which enhance its clarity. All parameters, including the noise process, have a clear physical meaning. We consider a slightly modified version of a previously presented model for the catalytic $A + 1/2B_2$ ($\text{CO} + 1/2 \text{O}_2$) reaction on Pt single crystal surfaces [6,7], which shows different types of kinetic oscillations in agreement with experimental results. Our model follows the one by Ziff, Gulari, and Barshad [15] (ZGB model) and is investigated by means of MC simulations [7]. The surface of the Pt catalyst is represented by a square lattice of side length L with the coordination number $z = 4$ and lattice constant $a = 1$. From experiment [5] it is known that kinetic oscillations are closely connected with the $\alpha \rightleftharpoons \beta$ reconstruction of the Pt surfaces. A (CO) is able to adsorb onto a free surface site with rate y and to desorb from the surface with rate k , independent of the surface phase to which the site belongs. B_2 (O_2) adsorbs dissociatively onto two nearest neighbor (NN) sites with rate $1 - y$ but different sticking coefficients s_α and s_β (see above). In addition A is able to diffuse via hopping onto a vacant NN site with rate D . The $A + B$ reaction occurs, if an A hops onto (i.e., tries to diffuse to) a site occupied by B , and the reaction product AB (CO_2) desorbs. All these processes are associated with the above kinetic transition

rates with dimension $[t^{-1}]$ of the stochastic model which therefore determine the relative speed of the individual reaction processes. For details, see Refs. [6,7,16].

The $\alpha \rightleftharpoons \beta$ phase transition is modeled as a linear phase border propagation with rate V . Consider two NN surface sites in the state $\alpha\beta$. The transition $\alpha\beta \rightarrow \alpha\alpha$ ($\alpha\beta \rightarrow \beta\beta$) occurs if none (at least one) of these two sites is occupied by A . Starting with a random heterogeneous distribution of the α and β phases the system develops a heterogeneous, dynamically stable state with oscillations, which are locally synchronized by A diffusion in a domain ξ . The α and β phases build almost homogeneous islands on a mesoscopic length scale. The oscillations remain local, interfere, and cancel each other on sufficiently large surfaces [6,7].

The nucleation is modeled as a spontaneous $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ phase transition of a single site with rate γ , completely independent of its neighbors or a particle adsorbed on this site. Therefore this nucleation process corresponds to a weak noise which generates dynamic defects on the surface. The term weak noise is used because the nucleation rate $\gamma \in [10^{-6}, 10^{-1}]$ is for the relevant values several orders of magnitude smaller than the other transition rates which are of the order of 10^{-1} to 10^3 . The defects grow or vanish via the $\alpha \rightleftharpoons \beta$ reconstruction depending on their chemical neighborhood, i.e., the presence or absence of A . It has to be emphasized that all phenomena, such as local oscillations, growth and decline of the heterogeneous distributed surface phase islands, quasiperiodical and chaotic behavior, exist even without the consideration of the nucleation process. As has been shown in Ref. [17] the nucleation process leads to SR. In this Letter we show that the nucleation can amplify the synchronization and that macroscopic synchronized oscillations develop without GC via the gas phase.

Let us first consider the system behavior in the absence of noise. During the course of the reaction in the $A + B_2/\text{Pt}(110)$ system a large A coverage induces the growth of a macroscopic β phase (state S1) almost completely covered with A , although a large B coverage is the "steady state" for S1. Because of A desorption a certain mean number of surface sites remains vacant. B_2 can adsorb. This then leads to a large density of randomly distributed B nuclei on the surface. The A coverage is then quickly removed via the $A + B$ reaction in a time $\Delta t \ll T$ which leads to further B_2 adsorption. Therefore the coverage of a large surface area is changed synchronously because of B_2 adsorption and $A + B$ reaction. This is not the case on Pt(100). Here β islands occur only in a macroscopic α phase and spatially separated domains covered by A and B always coexist. This has been confirmed by simulations of the $A + B_2/\text{Pt}(100)$ system including spontaneous nucleation in the context of the present work.

The fast removal of A is caused by B_2 adsorption. A diffusion plays only a minor role. Because of the large B coverage the α phase starts to grow and becomes

macroscopic (state S3) in time T . The dissociative B_2 dimer adsorption cannot completely cover the whole surface and vacant sites render possible further A adsorption. On the α phase only the A adlayer is stable and the change of the adsorbate layer from B to A again occurs very fast in time $\Delta t \ll T$. In time T the remaining β nuclei grow to a macroscopic β phase and the whole cycle starts over again.

These macroscopic oscillations in the surface phase coverage $\Theta_\beta = 1 - \Theta_\alpha$ cannot occur forever because an inherent mechanism of desynchronization exists. Consider state S1 with $\Theta_\beta \approx 1$ and $\Theta_\alpha \ll 1$ with the steady state B coverage $\Theta_B \approx 1$. In this case the remaining α islands start to grow with rate V . In this context it is important to note that these α islands are homogeneous and of a mesoscopic size, $N_\alpha \gg 1$. Therefore the individual α sites are not randomly distributed. For the density of α islands $\rho_\alpha = \Theta_\alpha/N_\alpha$ holds. The mean distance between these islands is given by $R_\alpha^0 = \rho_\alpha^{-1/2}$. The macroscopic $\alpha \rightleftharpoons \beta$ transition is possible only if this distance can be reached via phase border propagation, i.e., if $VT \sim R_\alpha^0$ is fulfilled. The same holds for state S3 with $VT \sim R_\beta^0$. The small number of the initial phase islands is subject to large fluctuations. As a consequence also the distances between such islands show large variations. Therefore the two conditions given above cannot be fulfilled for a long time. This then drives the system from global into local oscillations.

In the above scenario only the residual islands of the former macroscopic phase are able to act as nuclei for the surface phase transition, i.e., a real spontaneous nucleation has been neglected so far. We now consider spontaneous nucleation as a weak noise process as described above. We start with a macroscopic β phase covered by A . In this case the β phase is almost insensitive to the spontaneous $\beta \rightarrow \alpha$ nucleation because the large A coverage very quickly gives rise to the $\alpha \rightarrow \beta$ reconstruction. The nucleation with rate γ creates dynamic defects as potential nuclei with density $\rho = \gamma/V \ll 1$ which follows from $d\rho/dt = \gamma - V\rho$ for $t \rightarrow \infty$. The mean distance between these defects is given by $R = \sqrt{V/\gamma}$. If the chemical coverage now changes quickly from A to B the β phase becomes unstable and the defects (nuclei of the α phase) begin to grow. A macroscopic α phase can develop in time T if the synchronization condition $VT \sim R$ is fulfilled because T is almost completely determined by the slow process of the surface phase propagation. The same holds for the growth of β islands in a macroscopic α phase. The investigation of the spontaneous nucleation in a simulation is therefore only possible for $R < L$.

In the model without spontaneous nucleation the residual islands with mean distance R_α^0 or R_β^0 act as nuclei for the growth of the new macroscopic phases. For $R < R_\alpha^0$ and $R < R_\beta^0$ the spontaneous nucleation plays an important role. It has been shown in Ref. [7] that the oscillation period is given by $T \approx k^{-1}\sqrt{D/V}$. Because oscillations

occur only for values of $k \sim 10^{-1}$ [6] we can use this value of k as a constant. With $R = \sqrt{V/\gamma}$ and $VT \sim R$ we get $\gamma \sim k^2 D^{-1}$, i.e., in a system with physically reasonable diffusion rates a weak nucleation is sufficient to create defects at distances $R < \xi$ with $\xi = \sqrt{DT}$. These defects can then be synchronized by diffusion resulting in macroscopic globally synchronized oscillations in the surface phases, because only the individual adjacent phase nuclei have to be connected via A diffusion. As a consequence the normal condition $\xi \gg L$ for global synchronization is removed and the much weaker condition $\xi \gg R$ has to be fulfilled instead (with $R < L$ as an additional condition, of course, because otherwise $\xi > L$ holds and the influence of spontaneous nucleation cannot be seen). In our model we use $D = 100$ which leads to a value of $\gamma \sim 10^{-4}$. In Ref. [17] the present system has shown a SR maximum at $\gamma \in [10^{-4}, 10^{-2}]$. For $V = 1$ one gets $R \sim 10^2$ which enables simulations even on small lattices with $L > 100$. Therefore global synchronization via A diffusion can be obtained on lattices of arbitrary side length even for medium diffusion rates, as shown in Fig. 1. This has been verified for lattices up to $L = 8192$ in our simulations.

With $\xi = \sqrt{DT} > R$ there exists a lower limit for the diffusion rate D . For $D > k^{-2}V^3$ global synchronization is possible via the diffusive connection of adjacent phase nuclei at the distance R , i.e., if the system shows global synchronization for a certain value of V it is possible to remove the phenomenon of SR by simply increasing the surface phase propagation velocity V , as shown in Fig. 2. In this case R increases as $R = \sqrt{V/\gamma}$ until the condition $\xi > R$ for global synchronization is violated.

For reasons of comparison we also simulate the case of GC via the gas phase. For this purpose we assume that the adsorption and desorption of A immediately effects the gas phase concentration y of A . If A desorbs from or adsorbs onto the surface the value of y increases or decreases, respectively. The variations Δy are limited to 6%, which

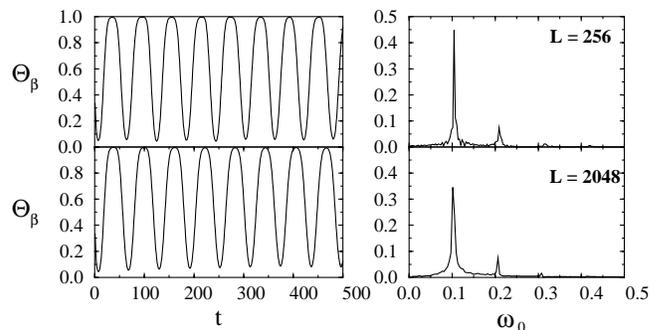


FIG. 1. Temporal oscillations (left) and power spectra (right) of the β phase coverage, Θ_β , for the simulation of the $\text{CO} + \text{O}_2/\text{Pt}(110)$ system on lattices with different side lengths L . The other parameters are kept constant at $y = 0.51$, $k = 0.1$, $D = 100$, $V = 1$, and $\gamma = 10^{-3}$.

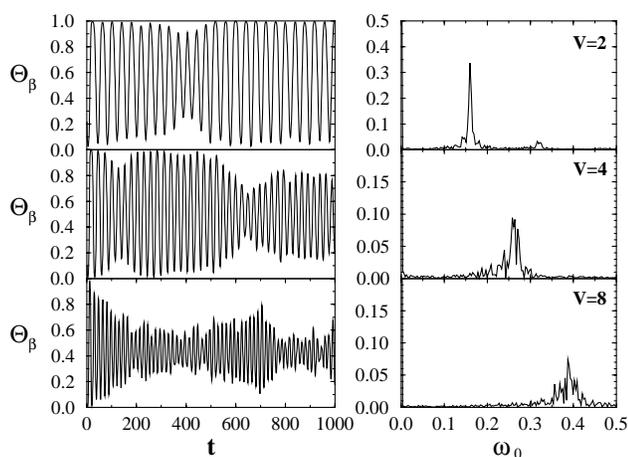


FIG. 2. Temporal oscillations (left) and power spectra (right) of the β phase coverage, Θ_β , for the simulation of the CO + O₂/Pt(110) system with different phase propagation rates V (for $V = 1$, see Fig. 1). The other parameters are kept constant at $y = 0.51$, $k = 0.1$, $D = 100$, $\gamma = 10^{-3}$, and $L = 256$.

is of the order of the experimentally measured CO pressure variations. At first we neglect spontaneous nucleation in order to investigate the influence of the GC. From Fig. 3 we see that oscillations develop but they are irregular and unstable. This appears to rule out this mechanism. If one includes in addition nucleation regular and synchronized oscillations develop in y as found in experiments.

In conclusion we have shown that the mechanism of GC via the gas phase, where local reactions are supposed to induce globally varying partial pressures of the reactants, can hardly be held responsible to lead to globally synchro-

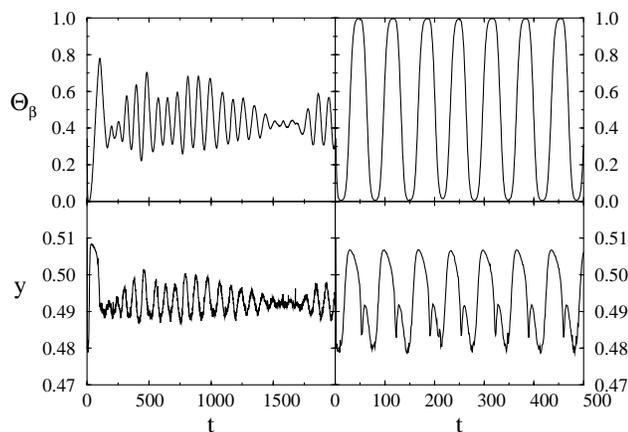


FIG. 3. Temporal oscillations in the simulation of the gas phase coupling with no nucleation (left) and with nucleation (right, $\gamma = 10^{-3.5}$). The β phase coverage, Θ_β (top), and the actual value of y (bottom) are shown for the simulation of the CO + O₂/Pt(110) system. The other parameters are kept constant at $y = 0.51$, $k = 0.1$, $D = 100$, $V = 1$, and $L = 2048$.

nized oscillations. The experimentally observed pressure variations [9] are the consequence and not the cause of a globally synchronized reaction on the surface. The surface reaction is globally synchronized by a weak noise process: the spontaneous nucleation of dynamic phase defects. One thus has the action of stochastic resonance. Because all processes (nonlinearity, periodic signal, noise) are internal to the system itself it is called *internal* stochastic resonance. This effect of noise might be regarded as counterintuitive, and to date, dynamic defects have always been considered as a disturbance of such a reaction system, but SR is by now a well-established phenomenon. In real reaction systems γ , V , and D should show an Arrhenius dependence on the temperature. Therefore one can expect that the resonance conditions can be fulfilled only in a very small parameter interval, as it has been shown for the real CO + O₂/Pt(110) reaction system. In the case of the disconnected Pd surfaces [14] one obtains two oscillators with large amplitudes and very similar or even equal frequencies. The pressure oscillations emerging via stochastic resonance from both surfaces can interact and easily synchronize each other.

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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