

## Delay-Induced Chaos in Catalytic Surface Reactions: NO Reduction on Pt(100)

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Deterministic chaos has been observed in the NO + CO and NO + H<sub>2</sub> reactions on Pt(100). A mathematical model is proposed that explains the origin as being due to delays in the response of a population of reacting adsorbate islands globally coupled via the gas phase. The dynamical equations of this model yield a sequence of period-doubling bifurcations resulting in chaos.

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Due to the conceptual simplicity of single crystal experiments, catalytic oscillatory chemical reactions on such surfaces have been intensively studied, and mathematical models which successfully reproduce most of the essential experimental facts have been constructed [1]. It may therefore appear as a surprise that, so far, no model explaining the occurrence of deterministic chaos found in several reaction systems, such as Pt(110)/CO + O<sub>2</sub> [2], Pt(100)/NO + H<sub>2</sub> [3], and Pt(100)/NO + CO [4], has been developed [5]. This failure simply reflects the fact that the origin of chaos in these surface reactions has not been well understood.

Most of the difficulties can be attributed to the fact that the role of the spatial degrees of freedom is unclear. For this reason we chose to investigate a system which has been shown to react spatially uniformly on a macroscopic scale ( $>1 \mu\text{m}$ ). This is the case for the rate oscillations we observe in the NO + CO and NO + H<sub>2</sub> reactions on the hex-reconstructed Pt(100) surface, e.g., on Pt(100)-hex [4].

In this paper we present a model that links the existence of chaotic behavior in the NO + CO and the NO + H<sub>2</sub> reactions on Pt(100) to delays in the response of a population of microscopic adsorbate islands to partial pressure variations in the gas phase. These variations control the nucleation rate of  $1 \times 1$  islands in the hex  $\rightarrow$   $1 \times 1$  phase transition, thus providing a very efficient synchronization mechanism for the oscillating surface which forms the basis of the model discussed below. The NO reducing reactions on Pt(100) have been studied mechanistically in quite some detail [1,6], but the idea we followed here was to incorporate only those mechanistic steps that are essential for the synchronization process and that are based on experimental facts.

The clean Pt(100) surface in its stable state exhibits a quasihexagonal reconstruction ("hex"), which can be reversibly lifted by an adsorbate like CO or NO, thus constituting an adsorbate-induced surface phase transition  $1 \times 1 \rightleftharpoons \text{hex}$  [7]. Isothermal rate oscillations and deterministic chaos have been found in both reaction systems under very similar conditions at low pressure

( $10^{-6}$ – $10^{-5}$  mbar) [3,4]. In a  $T$ -cycle experiment, oscillations occur on the cooling branch in the region of the phase transition as the increase in coverage with decreasing  $T$  causes a lifting of the hex reconstruction. The rate oscillations proceed on a largely hex reconstructed surface. They are coupled to the  $1 \times 1 \rightleftharpoons \text{hex}$  phase transition which modulates the catalytic activity, because only the  $1 \times 1$  phase dissociates NO, whereas the hex phase is inactive [4,6]. As demonstrated by the bifurcation diagram in Fig. 1, in the NO + CO reaction the rate oscillations develop via small amplitude chaotic oscillations which then transform with decreasing  $T$  into regular period-1 oscillations, going through a Feigenbaum cascade in the reverse direction [4].

Although spatially resolved measurements with photoemission electron microscopy (PEEM) revealed that the surface in the NO + CO reaction is oscillating spatially uniformly on a macroscopic scale ( $>1 \mu\text{m}$ ) [4], this

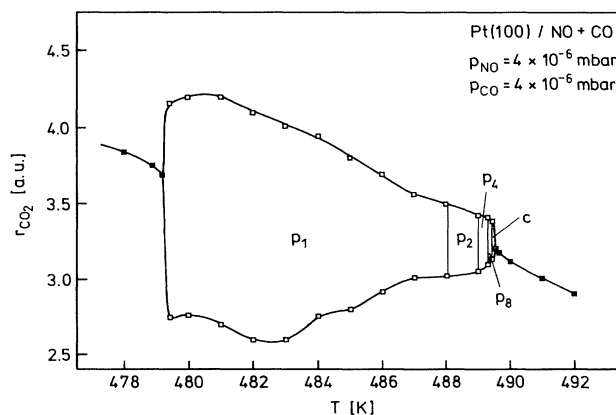


FIG. 1. Experimental bifurcation diagram for the rate oscillations in the NO + CO reaction on Pt(100)-hex [4]. Filled squares mark a stationary CO<sub>2</sub> production rate  $r_{\text{CO}_2}$ , while the open squares mark the upper and lower turning points of the rate oscillations.  $P_1$ ,  $P_2$ ,  $P_4$ , and  $P_8$  represent the periodicities that were identified in the experiment;  $C$  marks the region where chaotic oscillations were found.

homogeneity no longer exists on a microscopic scale. As shown by studies with LEED and scanning tunneling microscopy (STM) the adsorbate in the hex  $\rightarrow 1 \times 1$  phase transition is forced into  $1 \times 1$  islands with a local coverage of 0.5, while the surrounding hex area is largely adsorbate free [7–9]. Molecular beam studies of the CO-induced lifting of the hex reconstruction by King *et al.* demonstrated that the growth rate for the  $1 \times 1$ -CO islands,  $r_{\text{grow}}^{1 \times 1}$ , obeys a power law of the form  $r_{\text{grow}}^{1 \times 1} \sim (\theta_{\text{CO}}^{\text{hex}})^\nu$ , in which  $\theta_{\text{CO}}^{\text{hex}}$  denotes the CO coverage on the hex phase [10,11]. A value of  $\nu = 4.5$  was determined for  $T \approx 400$  K. One consequence of this power law is that small variations of  $p_{\text{CO}}$  can very strongly modulate the  $1 \times 1$  growth rate. Since mass balance in the reaction generates such small partial pressure variations (typically 1% of  $p_{\text{CO}}$  and  $p_{\text{NO}}$ ) a global coupling mode is present in a gradient-free flow reactor, which can very efficiently synchronize the oscillating surface via this critical dependence.

Coadsorbed NO and CO on the  $1 \times 1$  phase have been observed to react in an “explosive” way upon heating, yielding the products  $\text{CO}_2$  and  $\text{N}_2$  [6,12]. The “explosive” character was traced back to an autocatalytic reaction, which is ignited when the combined NO-CO coverage falls below the inhibition coverage of 0.5 for NO dissociation. Since the growth of the  $1 \times 1$  islands proceeds with the same local coverage of 0.5, the stability of the mixed  $1 \times 1$ -CO,NO island will be on a critical borderline, and we can construct the following life cycle for these islands. Starting with the bare hex phase,  $1 \times 1$ -NO,CO islands nucleate, and then grow as unreactive islands with a constant rate until they reach a certain critical size, where they become reactive. The adsorbate is reacted away, and, since the bare  $1 \times 1$  surface is no longer stabilized by the adsorbate, the structure relaxes back into the hex reconstructed surface.

If we furthermore assume that the individual islands, which initially nucleate randomly and grow isolated from each other, have to synchronize in order to produce macroscopic variations of the reaction rate, all essential parts of our model for the occurrence of chaos are present. Neglecting differences between NO and CO, which behave very similarly with respect to the phase transition, we arrive at a set of three differential equations describing the variations in the CO-NO pressure,  $p$ , the NO-CO coverage on the hex phase,  $c$ , and the reactive  $1 \times 1$  area,  $q$ :

$$\dot{c} = -\gamma c + \alpha p(1 - c), \quad (1)$$

$$\dot{p} = -\Gamma(p - p_0) - kpq, \quad (2)$$

$$\dot{q} = -\mu q + w. \quad (3)$$

Equation (1) represents the adsorption and desorption of NO/CO on the hex phase with  $\gamma$  denoting the desorption constant. Equation (2) is a reactor equation of the continuously stirred tank reactor (CSTR) type, in which

the reactor is characterized by the inverse of the reactor residence time,  $\Gamma$ , and the reaction rate is given by the product  $kpq$ . Equation (3) describes the variation in the reactive  $1 \times 1$  area. The first term represents the activated relaxation of the reactive  $1 \times 1$  area into the hex phase. The second term  $w$  denotes the rate of appearance of new reactive  $1 \times 1$  area:

$$w(t) = Ac(t - \tau)^\nu p(t - \tau)q(t - \tau). \quad (4)$$

Since the adsorbate islands become reactive only when they reach a critical size corresponding to a critical age  $\tau$ , the growth rate for the reactive  $1 \times 1$  area is proportional to the nucleation rate for  $1 \times 1$  islands at the *delayed* time moment  $t - \tau$ . In the expression for  $w$ , the experimentally determined power law dependence  $c^\nu$  for the  $1 \times 1$  growth rate has been incorporated [10,11]. Since it is known that the NO + CO reaction leads to a significant roughening of the Pt(100) surface, we assume that heterogeneous nucleation is dominant and set the mean nucleation rate proportional to the reaction rate  $kpq$  [13]; the remaining coefficient  $A$  combines several proportionality factors.

Under the conditions of our experiment the desorption rate  $\gamma$  is much larger than the adsorption rate, and the coverage  $c$  remains small ( $c \ll 1$ ). The coverage then adiabatically adjusts to the partial pressure variations and Eq. (1) yields  $c = (\alpha/\gamma)p$ . Introducing dimensionless variables  $x = p/p_0$  and  $y = kq/\Gamma$  and measuring the time  $t$  in units of the delay  $\tau$ , we reduce (1)–(4) to a system of two equations:

$$G^{-1}\dot{x} + x = 1 - xy, \quad (5)$$

$$g^{-1}\dot{y} + y = a[x(t - 1)]^r y(t - 1), \quad (6)$$

where the coefficients are  $G = \Gamma\tau$ ,  $g = \mu\tau$ ,  $r = \nu + 1$ , and  $a = A\alpha^\nu p_0^{\nu+1}/\mu\gamma^\nu$ .

Some insight into the dynamical properties of this model can be obtained by considering the singular limit  $G \rightarrow \infty$ ,  $g \rightarrow \infty$  where the equations reduce to the iterative map

$$y(t + 1) = \frac{ay(t)}{[1 + y(t)]^r}. \quad (7)$$

This map exhibits a transition to chaos through a sequence of period-doubling bifurcations [14]. The previous analysis of other dynamical systems with time delays, describing complex physiological oscillations [15] and the effects of optical bistability [16,17], has shown that the behavior of such a system could be very close to that found in the singular limit for a respective discrete map. A similar behavior might thus be expected in our case.

We have performed numerical simulations of the system (5) and (6). Using data from the literature, the exponent  $r$  was estimated to be  $\approx 10$  at  $T = 480$  K [10]. The delay time  $\tau$ , which could not be directly measured, has been chosen in such a way that the experimental

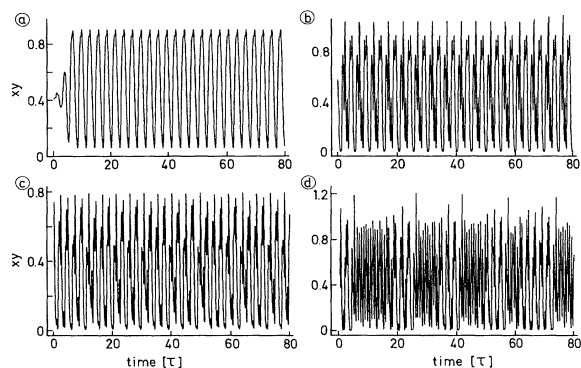


FIG. 2. Oscillations in the dimensionless reaction rate  $xy$  obtained by numerical integration of Eqs. (5) and (6) with the parameters  $G = 16$ ,  $r = 10$ , and (a)  $a = 240$ ,  $g = 3$ , (b)  $a = 160$ ,  $g = 7$ , (c)  $a = 52$ ,  $g = 8$ , (d)  $a = 100$ ,  $g = 10$ . Time is measured in units of the delay time  $\tau$ .

oscillation period is reproduced. Figure 2 shows the time dependence of the quantity  $xy$ , which is proportional to the reaction time  $kpq$  for different parameter values  $a$  and  $g$ . We see that the system demonstrates simple limit-cycle oscillations [Fig. 2(a)], stable oscillations with higher periods [Figs. 2(b) and 2(c)], and complex irregular oscillations [Fig. 2(d)]. The computation of the maximal Lyapunov exponent for such complex oscillations shows that the exponent is positive ( $\lambda \cong 0.2$ ), and therefore they can be described as chaotic.

By repeating the simulations for various choices of the parameters, we have constructed an approximate bifurcation diagram for the dynamical system (5) and (6) in the  $(a, g)$  plane, which is displayed in Fig. 3. Inside the grey region in Fig. 3, complex oscillations with high periods and chaotic oscillations are observed (the fine

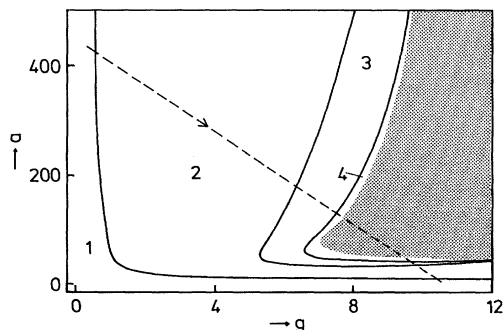


FIG. 3. Approximate bifurcation diagram for the dynamical system (5) and (6) for  $G = 16$  and  $r = 10$ ; (1) stable steady state, (2) period-1 oscillations, (3) period-2 oscillations, (4) period-4 oscillations. Complex oscillations and chaotic regimes are found inside the grey region. The dashed line with the arrow schematically shows how this diagram is traversed with increasing temperature.

structure of this region has not been fully resolved in our simulations).

In order to establish a correspondence between Fig. 3 and the experimental bifurcation sequence in Fig. 1, we notice that, when the temperature grows, both the desorption rate  $\gamma$  and the rate of the  $1 \times 1 \rightarrow$  hex phase transition  $\mu$  increase. Since the parameter  $a$  in (5) is proportional to  $\mu^{-1}\gamma^{-\nu}$  with  $\nu = 9$ , it has to decrease rapidly with temperature. On the other hand, the parameter  $g$  is proportional to  $\mu$  and therefore slowly grows with temperature. Hence, as the temperature is gradually increased, the bifurcation diagram in the plane  $(a, g)$  is traversed in the direction schematically indicated by the dashed line in Fig. 3.

We see that, in agreement with the experimental data, simple period-1 oscillations occupy a relatively wide interval. Undergoing period doublings, they are transformed into chaotic oscillations. The inverse sequence of bifurcations leading to a stable steady state occurs rapidly when the system leaves the chaotic region. In the experiment, the transition to a steady state above the chaotic window could not be resolved, which we attribute to the smallness of the parameter region and the low amplitude of the chaotic oscillations. Although the model presented here is a skeleton model and neglects all details of the reaction, it reproduces the dynamical behavior found in the NO + CO and the NO + H<sub>2</sub> reaction on Pt(100)-hex [3,4]. The fact that both systems exhibit similar dynamical behavior already demonstrates that details of the chemistry cannot be important for creating chaotic behavior. Also note that experiments with two different Pt(100) single crystals yielded exactly the same sequence of period doublings in the NO + CO reaction, thus ruling out a possible influence of macroscopic defects or other irregularities [18].

In conclusion, we have shown that deterministic chaos in catalytic surface reactions can have its origin in a failure of the synchronization process as the delay between global coupling and the response of the surface reactions begins to dominate the dynamics. Since this can occur in many other synchronized reaction systems, such a mechanism leading to chaos will be also relevant there.

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