Oscillatory CO oxidation on Pt(110): Modeling of temporal self-organization

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The parameters entering the kinetics for the mechanism of catalytic CO oxidation have been adapted for a Pt(110) surface, giving rise to a two-variable model correctly predicting bistability. Oscillations are obtained when, in addition, the adsorbate-driven $1 \times 2 - 1 \times 1$ structural phase transition of Pt(110) is taken into account. Mixed-mode oscillations can be qualitatively explained by including the faceting of the surface as a fourth variable. The limitations of the model essentially stem from the fact that only ordinary differential equations have been analyzed so far neglecting spatial pattern formation. It is discussed which dynamic phenomena observed experimentally in the CO oxidation on Pt(110) will probably not be adequately describable without taking spatial effects into account.

I. INTRODUCTION

Phenomena of nonlinear dynamics have been studied extensively in the CO oxidation on a variety of catalysts and under different conditions (see, e.g., Ref. 1), among these also detailed experiments under isothermal low-pressure conditions on well-defined single crystal surfaces (see Refs. 2-4 for recent reviews). In these studies bistability, but no oscillations, were found for Pt(111), whereas sustained oscillations were obtained for the Pt(100) (Ref. 6) and (110) surfaces. For the latter, also complex temporal behavior such as mixed-mode oscillations, period-doubling transition to chaos, and even hyperchaos were observed. The formation of stationary as well as propagating spatial patterns has also been studied on Pt single crystal surfaces, but will not be the subject of the present paper; rather we shall concentrate on those aspects that can be described without taking spatial effects into account and discuss the limitations of the model afterwards.

Surface science techniques provide powerful tools to investigate the elementary steps of a catalytic reaction. In the case of Pt single crystal surfaces it was shown that the densely packed Pt(111) surface exhibits the same structure as the bulk ($1 \times 1$), whereas the clean (100) and (110) surfaces are reconstructed, exhibiting a $5 \times 20$ (“hex”) resp. $1 \times 2$ (“missing row”) structure. The reconstructions can be lifted (i.e., the $1 \times 1$ forms) by chemisorption of a number of gases. Such single crystal studies turned out to be useful in elucidating the mechanism responsible for the occurrence of bistability and oscillations. Thus in-situ low-energy electron diffraction (LEED) studies showed that oscillations on Pt(100) and (110) are accompanied by periodic changes of the surface structure between the $1 \times 1$ and the respective reconstructed phase. Such structural changes, in turn, influence the velocity of other elementary processes. For not too high temperature, further structural changes of the (110) surface were observed for ongoing reaction, namely, the formation of new crystal planes (faceting) which substantially changes the adsorption properties of the crystal, in particular with respect to oxygen.

The present paper presents a kinetic model to describe the temporal dynamics on the Pt(110) surface. The rate constants and parameters needed in the equations have been determined by different groups using a variety of surface science techniques and are critically reviewed in Sec. III. Afterwards, the model is developed stepwise, i.e., it is at first kept as simple as possible, then more effects and variables are taken into account in order to describe dynamic behavior of increasing complexity (and embedding dimension) of the CO oxidation on Pt(110).

II. COMPUTATIONAL METHODS

The computations were carried out on a VAX 6800 and a VAX station 3100, always in double precision FORTRAN.

Numerical integration was done using routines for stiff systems of ordinary differential equations (ODEs) with explicit Jacobian (D02Exx from NAG 13), which are based on backward differentiation formulas. Bifurcations were located with standard one- and two-parameter continuation techniques using a linear predictor and Newton’s method as corrector; the stepsize for the predictor was mostly only varied (and reversed) near turning points.

For convenience, the notation used for the various bifurcations which were encountered in the present study is compiled in Table I.

Continuation of limit cycles was performed using a plane in phase space on which one of the variables has a constant value as Poincaré section. The system was then integrated until the variable in question had reached this value twice. The Jacobian of the fixed points of this mapping was obtained by simultaneous integration of the time derivatives of its elements. The sl bifurcations were followed by continuation of a large-period limit cycle using E. Doedel’s AUTO package. In order to accurately determine the location of an NSL point it turned out advantageous to also compute the curve of a neutral saddle (which intersects the sl transversally at the NSL).

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TABLE I. Bifurcations and abbreviations used in the present paper.

<table>
<thead>
<tr>
<th>Codimension 1</th>
<th>s</th>
<th>sn</th>
<th>h</th>
<th>h'</th>
<th>sl</th>
<th>snl</th>
<th>NSL</th>
<th>DH</th>
</tr>
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<tbody>
<tr>
<td>Cur.</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Codimension 2</td>
<td>C</td>
<td>cusp</td>
<td>sn/sn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TB</td>
<td>Takens–Bogdanov</td>
<td>sn/h</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>SNL</td>
<td>Saddle-node loop</td>
<td>sn/sl</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NSL</td>
<td>Neutral-saddle loop</td>
<td>sl/snp</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>DH</td>
<td>Degenerate Hopf</td>
<td>h/snp</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Codimension 3</td>
<td>TBC</td>
<td>Takens–Bogdanov cusp</td>
<td>TB/C</td>
<td></td>
<td></td>
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</table>

No three-parameter continuations were carried out. However, two-parameter bifurcation diagrams were computed at different values of a third parameter so that indirect evidence for phenomena of codimension 3 could be obtained (see Sec. IV C).

The experimental procedures have been described in detail elsewhere.8,27

III. DETERMINATION OF THE KINETIC PARAMETERS

The overall reaction mechanism of CO oxidation on Pt is well established; both reactants have to adsorb before the reaction takes place (Langmuir–Hinshelwood mechanism, cf. Sec. IV). On Pt(100) and (110) the surface reconstruction has to be taken into account also.

There are numerous studies reported in the literature about the interaction of CO and/or O2 with Pt(110) using a variety of surface science techniques. We have reproduced some of this work in order to determine the rate constants required for a model, especially in cases where there were discrepancies between different literature values or where the data reported by other authors were taken under conditions not comparable to those under which oscillations occur.

A. CO adsorption

Although in a few studies21,28 a sticking coefficient slightly smaller than 1 was reported, most authors agree that the initial sticking probability $s_c$ (Refs. 18, 29, and 30) and the saturation coverage $\nu_s$ (Refs. 18, 21, 29, and 31–33) are both equal to unity (which has been corroborated by our measurements).8

The sticking coefficient does not noticeably decrease for small CO coverages, but remains approximately constant until a coverage $u$ of 0.3,28 respectively 0.5.18 This precursor effect can be described after Gasser and Smith [Eq. (1)]34 or after Kisliuk [Eq. (2)].35

$$s(u) = 1 - u^q,$$

$$s(u) = \left(1 + \frac{uK}{1 - u} \right)^{-1}.$$  

Comrie and Lambert29 used (1) and obtained a mobility parameter $q$ of 4; in agreement with our result of $3.5 \pm 0.5$ (Ref. 8). With the Kisliuk model $K$, around 0.2 was obtained for our data, but the fit was not as good so that it seems more appropriate to use the ansatz of Gasser and Smith.

It turned out that the computations were not very sensitive to $q$. Even neglecting the precursor altogether ($q = 1$) did not qualitatively alter the results.

B. CO desorption

The thermal desorption spectra of CO on Pt(110) consist of two peaks $\alpha$ and $\beta$.8,21,29,34 In order to compute the heats of adsorption $E_{d\alpha}$ and $E_{d\beta}$ the preexponential factor $k_d$ is required; the estimate of $10^{13}$ s$^{-1}$ (Refs. 29 and 36) appears much too small. Using $6 \times 10^{14}$ s$^{-1}$ (taken from an MBRS study)28 in the Redhead equation37 gives $E_{d\alpha}$ of around 30, and $E_{d\beta}$ of nearly 40 kcal/mol for all TDS studies (see Ref. 8). The isosteric heat of adsorption strongly depends on coverage and decreases for $u > 0.5$.18

For the model calculations, parameters realistic around a coverage of 0.5 are required. Since the 1×2→1×1 phase transition of the surface is completed for a CO coverage of 0.5,18,19,21,33,38 the disappearance of the 1×2 spots in the LEED pattern in a CO atmosphere could be used to probe the CO adsorption/desorption equilibrium around this coverage.8 We obtained a preexponential factor of > $10^{16}$ s$^{-1}$ and a heat of desorption as $E_{d\alpha}$ mentioned above. These data were used in the computations. The coverage dependence of the heat of adsorption was mostly neglected in order to keep the equations reasonably simple. While this did not alter the qualitative features of the model, assumption of a coverage dependence following Jackman et al.15 significantly improved the fit of the bistable region (see Sec. IV A, Fig. 2).

C. O2 adsorption

Dissociative adsorption of oxygen was found to proceed via second order kinetics in the free sites in several studies.8,39,40 The reported initial sticking coefficients range from 0.13 (Ref. 39) to 0.6,8 the best estimate is considered to be about 0.4, a value close to which the other results are scattered.20,40,41

Saturation coverages have been determined using x-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES) by several groups. At room temperature the 1×2 phase saturates between 0.3 and 0.35,19,20,40 the 1×1 at 0.8.30 At elevated temperatures the coverage reaches 0.8 also for the 1×2 structure.8,39,42

Oxygen adsorption does not noticeably influence the phase transition of the surface.8,19,20

TDS of oxygen on Pt(110) was reported in Ref. 39. From work function studies we concluded that there is no noticeable shift in the adsorption/desorption equilibrium below 700 K (Ref. 8) so that desorption was neglected in the calculations because only the behavior at lower temperatures is relevant for the dynamical phenomena to be modeled.
D. Coadsorption of CO and O$_2$

It is well known that the inhibition of adsorption of CO and O$_2$ is asymmetric on a number of catalytically active metals (see, e.g., Refs. 2–4 and references therein), insofar as preadsorbed CO blocks oxygen adsorption but not vice versa. Thus a state with high O (CO) coverage exhibits high (low) rate of CO$_2$ production. The asymmetric inhibition can be readily (albeit indirectly) established experimentally when slowly increasing $p_{CO}$ (from zero) at constant $p_{O2}$: The CO$_2$ production at first rises linearly with $p_{CO}$ (first order), then saturates, and drops sharply to a small value, when the surface becomes CO covered. In this region the rate becomes practically independent of the pressures (zeroth order). For high temperature no sharp drop occurs any more, since CO desorption increases significantly which leads to more empty sites allowing a higher reaction rate. For asymmetric inhibition on Pt(110) see the measurements reported in Ref. 8.

E. Surface reaction

The surface reaction between adsorbed CO and O is generally described as second order (i.e., proportional to both coverages). There are only few kinetic measurements available. Using a relaxation technique (modulation of temperature)\textsuperscript{43} the activation energy $E_r$, and the preexponential factor $k_0$ were found to depend strongly on the O coverage $v$; namely, 22 kcal/mol and $3 \times 10^{12}$ s$^{-1}$ for $v < 0.15$ resulted, while these values dropped to 8 kcal/mol resp. $10^5$ s$^{-1}$ for $v > 0.25$.\textsuperscript{43} Similar quantities were obtained earlier as fit parameters of a model (7.9 kcal/mol and $1.8 \times 10^4$ s$^{-1}$).\textsuperscript{44}

In order to obtain rate constants applicable under oscillatory conditions the occurrence of the surface phase transition in the presence of CO and O$_2$ was observed as a function of temperature. This should give reasonable results near a CO coverage of 0.5, where also the instabilities occurred in experiment.\textsuperscript{7,8}

The resulting Arrhenius plot gave an effective preexponential factor between $10^4$ and $10^5$ s$^{-1}$, and a slope of about 8 kcal.\textsuperscript{7} Although under these conditions it is expected that the coverages are mainly determined by the surface reaction, the other steps (namely, adsorption and desorption of CO) will, of course, also play a role. The curve was therefore fitted with a Langmuir–Hinshelwood mechanism, using the parameters for adsorption and desorption described above. The experimentally obtained effective rates could be well reproduced using a value of $10^6$ s$^{-1}$ for $k_0$ and 10 kcal/mol for $E_r$ (see Sec. IV, Figs. 2 and 3). It was not necessary to assume coverage-dependent parameters, which effect was therefore not included in the model, although it can clearly become important under different conditions (i.e., further away from the oscillatory region).

F. Phase transition

Upon chemisorption of CO, the $1 \times 2 \rightarrow 1 \times 1$ transition of Pt(110) has been shown to set in at a coverage of 0.2 (Refs. 38 and 45–47) (below which it is assumed that CO molecules exist as so-called singletons on the surface).\textsuperscript{21,47}

As already mentioned, the transition is completed at a coverage of 0.5. Between these two critical coverages an equilibrium degree of reconstruction monotinous and differentiable everywhere was assumed [which could readily be fitted with a polynomial of third order in $u$, see Eq. (4c) in Sec. IV B].

The relaxation to this equilibrium was again described with an Arrhenius-type rate. The activation energy $E_p$ can-

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TABLE II. Kinetic parameters entering the model [Eqs. (4a)–(4d)]; for experimental measurements see Sec. III; $k_i = k_0 \exp(-E_i/RT)$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO adsorption</td>
<td>$\kappa_i$ Rate of CO hitting surface</td>
<td>$3.135 \times 10^9$ s$^{-1}$ mbar$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$s_i$ Sticking coefficient</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$u_i$ Saturation coverage</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$q$ Mobility parameter of precursor adsorption</td>
<td>3</td>
</tr>
<tr>
<td>O$_2$ adsorption</td>
<td>$\kappa_0$ Rate of O hitting surface</td>
<td>$5.858 \times 10^5$ s$^{-1}$ mbar$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$s_0$ Sticking coefficient</td>
<td>$1 \times 2$: $s_{12} = 0.4$</td>
</tr>
<tr>
<td></td>
<td>$v_0$ Saturation coverage</td>
<td>$1 \times 1$: $s_{11} = 0.6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>Rates</td>
<td>$k_r$ Reaction</td>
<td>$k_0^r = 3 \times 10^9$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$k_d$ Desorption of CO</td>
<td>$k_0^d = 2 \times 10^{10}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$k_p$ Phase transition</td>
<td>$k_0^p = 10^5$ s$^{-1}$</td>
</tr>
<tr>
<td>Equilibrium $1 \times 1$</td>
<td>$r_i$ Polynomial coefficients for equilibrium value of phase transition</td>
<td>$r_3 = -1/0.0135$, $r_2 = -1.05r_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$r_1 = 0.3r_3$, $r_0 = -0.026r_3$</td>
</tr>
<tr>
<td>Facets</td>
<td>$k_f$ Rate of facet formation</td>
<td>$k_f = k_0^f = 0.03$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$k_t$ Rate of thermal annealing</td>
<td>$k_0^t = 2.65 \times 10^9$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$s_{03}$ Increase of $s_0$ for maximum faceting ($z = 1$)</td>
<td>$s_{03} = 0.2$</td>
</tr>
</tbody>
</table>
not be very high, since the process is known to occur on a
time scale of minutes at room temperature. A direct
determination of $E_a$ using LEED has been carried out by
Heinz et al., who found values slightly above 6 kcal. Using
their data (Figs. 2–4 in Ref. 48) preexponential factors from
40–800 s$^{-1}$ can be estimated (depending on the growth law
assumed). The values chosen (Table II) result in correct
time scales for the transition near the instability from room
temperature (several minutes) to $\sim 550$ K (a few seconds).

G. Faceting

The formation of new crystal planes on Pt(110) (faceting)
during CO oxidation exhibits complicated kinetics and
can certainly not be viewed as an elementary process. In the
present context it was only attempted to describe the overall effect of faceting on the dynamics. Therefore, a phenomenological expression for the degree of faceting was used, and rate coefficients were fitted for this expression, without trying to capture the details of the process.

The facets in the studies cited were found to develop in a
predominantly CO-covered state (after lifting of the recon­
struction), but only as long as there was noticeable turnover.
Over a wide range the velocity of faceting is approximately
independent of temperature; it takes $\sim 5$ min to reach
90% of the saturation level. The saturation degree of faceting
remains unchanged up to about 460 K, then drops sharply
to $\sim 50\%$ at 480 K and becomes unnoticeable around
555 K (the temperatures given are pressure dependent). The thermal annealing of facets strongly depends on temperature (several minutes) to $\sim 550$ K (a few seconds).

IV. DEVELOPMENT AND ANALYSIS OF THE MODEL

A. Bistability

The oxidation of CO on platinum is known to proceed
via the classical Langmuir–Hinshelwood (LH) mechanism
(see Refs. 53–55 and references therein),

$\bullet + CO \rightleftharpoons CO_{ad}$,  

$2\bullet + O_2 \rightarrow 2O_{ad}$,  

$CO_{ad} + O_{ad} \rightarrow 2\bullet + CO_2$.  

(Here $\bullet$ denotes an empty site, adsorbed species are written
with the subscript ad.) CO desorbs immediately at the tempera­
tures under consideration and therefore constitutes an inert product. The other gases exhibit only small variations of their partial pressure under the applied conditions so that they can be assumed constant. Thus, all gaseous species are nonessential (type b resp. c) in the sense of.

The experimentally observed asymmetric inhibition of the adsorption processes described in the previous section is not contained in the above scheme as it stands. Nevertheless, it is crucial to take this effect into account, which we did by appropriate choice of the inhibition factors [see Eqs. (4a) and (4b) below]. Failure of doing this would result in a

model not only giving quantitatively wrong turnover for CO
oxidation, but also predicting a physically implausible fixed point ("absorbing state"), where the reaction can be completely blocked by O$_{ad}$ with exactly vanishing CO coverage. Such states could also be avoided by the assumption that process (3c) is reversible (or, in general, that all adsorption processes are), which is, however, for quantitative reasons not the method of choice in CO oxidation.

Only three essential species remain, namely CO$_{ad}$, O$_{ad}$, and $\bullet$. Since they satisfy a conservation constraint in the above reaction scheme (the sum of their coverages equals unity), only two of them need to be computed. We chose CO$_{ad}$ and O$_{ad}$ and denote their coverages by $u$ and $v$, respectively. Four terms, namely those describing CO adsorption, CO desorption, O$_2$ adsorption, and the surface reaction have to be included (oxygen desorption is neglected, cf. Sec. III), which gives rise to the following differential equations:

\[
\dot{u} = p_{CO} \kappa_u (1 - u/u_s)^3 - k_u - k_w, \quad (4a) \\
\dot{v} = p_{CO} \kappa_v (1 - u/u_s - v/v_s)^3 - k_w. \quad (4b)
\]

Here $\kappa_u$ and $\kappa_v$ denote the rates with which the resp. adsorp­
tives hit the surface at unit pressure, computed from kinetic
gas theory assuming ideal behavior according to

\[
\kappa_i = N_A/\theta_M \sqrt{2\pi M_i RT},
\]

where $N_A$ is the Avogadro number, $\theta_M$ the number of sites in a monolayer, $M_i$ the molecular weight of gas $i$, and $T$ the gas temperature. $s_0 = 0.6$ was used.

The Eqs. (4a) and (4b) depend on three external (and experimentally readily accessible) control parameters, namely, the partial pressures $p_{CO}$ and $p_{O_2}$ as well as the crys­
tal temperature $T$, which enters through the Arrhenius ex­
pressions for $k_u$ and $k_w$ (Table II).

FIG. 1. Stationary oxygen coverage $v$ as a function of $p_{CO}$ and $T$ as computed from Eqs. (4a) and (4b) exhibiting bistability and a cusp; full (dashed) lines denote stable nodes (saddles); sn bifurcations occur along the parabo­
la-shaped full curve.

Analysis of the ODE system (4a) and (4b) reveals that there is bistability (hysteresis) in one, and a cusp in two control parameters, as shown in Fig. 1, where \( u \) is reproduced as a function of \( p_{CO} \) and \( T \). No further bifurcations (nor other limit sets) than those of Fig. 1 were found with this system anywhere in parameter space.

The experimental data in Fig. 2, where the (dis)appearance of the 1×2 spots in video LEED during temperature ramps is shown, clearly suggest a hysteresis broadening for lower \( p_{CO} \). The same effect was obtained when the \( CO \) production rate or the work function \( \Delta \varphi \) was monitored.\(^8\) For comparison the isostere \( u = 0.5 \) for \( p_{O_2} = 0 \), and the location of the sn curves have also been computed from the model [Fig. 3(a)]. It can be seen that the bistable region is much broader than observed (Fig. 2), but this discrepancy vanishes if the coverage dependence of \( CO \) desorption is taken into account [Fig. 3(b)].

The data reported by Jackman et al.\(^8\) can be approximated by a continuous curve for the isosteric heat of adsorption \( E_d \) as a function of coverage \( u \) of the form \( E_d = 38 - u^3(38 - 25) \). (This function is fairly arbitrary; quite similar results were obtained when the experimental data were fitted in a different way.)\(^9\)

**B. Simple oscillations**

Experimental data comparable to Fig. 1 are reproduced in Fig. 4, clearly exhibiting the general form of a cusp. However, the vertical bars indicate the highest amplitude of oscillations at the respective temperature. Thus, experimentally there was a narrow oscillatory region (2%-12% in \( p_{CO} \)) inseparably close to the bistable one. This becomes clear from the measurement reproduced in Fig. 5, where upon stepwise increase of \( p_{CO} \), a sharp drop of \( \Delta \varphi \) occurred at a certain point (indicating an sn) close to which oscillations resulted when \( p_{CO} \) was lowered slightly. These oscillations resulted when \( p_{CO} \) was lowered slightly. These oscillations

![Fig. 2](image-url)  
**FIG. 2.** In \( p_{CO} \) vs 1/T plot of the completion of the 1×2→1×1 phase transition of Pt(110) in comparison to oscillation conditions (cf. Refs. 5 and 56). Crosses: values where the transition is completed in CO alone; no hysteresis occurred in these measurements. Triangles: phase transition in the presence of CO and \( 5.3\times10^{-5} \) mbar \( O_2 \). Triangles standing on an edge (corner) denote the beginning of the 1×1→1×2 (completion of 1×2→1×1) transition while increasing (decreasing) the crystal temperature. Note the considerable hysteresis towards lower \( T \).

![Fig. 3](image-url)  
**FIG. 3.** Isostere \( u = 0.5 \) with \( p_{O_2} = 0 \) (steep curve to the left) and location of sn bifurcations for \( p_{O_2} = 5.3\times10^{-5} \) mbar computed from Eqs. (4a) and (4b); (a) coverage-independent CO desorption; (b) isosteric heat \( E_d \) of CO decreases for increasing \( u \) down to 25 kcal/mol according to \( E_d = 38 - u^3(38 - 25) \). In both cases the sn curves meet in a cusp at high \( T \), where the bistable area vanishes (cf. Fig. 2).

![Fig. 4](image-url)  
**FIG. 4.** Work function \( \Delta \varphi \) of Pt(110) at constant oxygen pressure in dependence of the parameters \( p_{CO} \) and \( T \). Vertical bars indicate the highest oscillation amplitudes obtained at the respective temperature which are almost as large as the discontinuity due to bistability (cf. Fig. 1).
FIG. 5. Change of $\Delta \varphi$ vs time during stepwise increase of $p_{CO}$. There is a sharp jump in $\Delta \varphi$ from $\alpha$ to $\beta$, after which a small reduction of $p_{CO}$ leads to oscillatory behavior. ($T = 505 \text{ K}, p_{O_2} = 7 \times 10^{-4} \text{ mbar}, p_{CO} = 0, 7, 20, 40, 55, 75, 95, 115 \text{ (a)}, 125 \text{ (b)}, 120 \text{ (osc)} \times 10^{-4} \text{ mbar}$).

FIG. 7. Example of oscillations obtained by integration of Eqs. (4a)-(4c) ($T = 540 \text{ K}, p_{CO} = 3 \times 10^{-7} \text{ mbar}, p_{O_2} = 6.67 \times 10^{-7} \text{ mbar}$); $u$ and $v$ oscillate in a strictly anticorrelated way, the slow variable $w$ reaches its maximum after $u$.

are not predicted by the simple model (4a) and (4b). Consequently, some other effect has to be taken into account, namely the structural phase transition of the Pt(110) surface. Figure 6 shows the equilibrium $1 \times 1$ coverage $w_0$ as a function of $u$ (as obtained from a polynomial fit, see Sec. III) in comparison with experimental data. A third differential equation describing the relaxation of the surface structure to its equilibrium value was added to the model.

FIG. 8. Skeleton bifurcation set of the reconstruction model of surface oscillations [Eqs. (4a)-(4c)] for $T = 540 \text{ K}$. The sn bifurcations (full lines) enclose a region where three stationary states coexist, Hopf bifurcations occur along the dashed line. The region in which a stable limit cycle exists is indicated by stripes.
The oxygen sticking coefficient $s_0$ was taken as a linear combination of the values for the $1 \times 2$ and $1 \times 1$ structure $s_0 = w s_{01} + (1 - w) s_{02}$. The ODE system (4a)-(4c) indeed exhibited oscillations, a time series is shown in Fig. 7.

A bifurcation diagram in two parameters, $P_{CO}$ and $P_{CO}$, at 540 K is reproduced in Fig. 8. The dashed area marks the existence of a stable limit cycle. It is quite narrow in the region of three coexisting fixed points (only close to the Hopf bifurcation), while a broader oscillatory regime resulted adjacent to this region. At low pressure the Hopf bifurcation emanated from a TB point so close to the cusp that it cannot be separated with the scale used, while for higher pressure it terminated in a second TB point (cf. Fig. 9). Also, at high pressure the bistable region closed in another cusp. All bifurcations of codimension 1 shown in this figure have also been detected experimentally: The sn bifurcations cause hysteresis resp. sharp jumps in the measurements; the Hopf bifurcations manifest themselves in a continuous increase of the oscillation amplitude with the control parameter; for slightly higher pressure the oscillatory region is only on one side bounded by a Hopf bifurcation, while on the other end a sniper occurs (Fig. 8), which leads to very large (and finally diverging) oscillation period, due to an increasingly long single steady phase of the limit cycle. This effect has recently also been observed experimentally. Also, in agreement with experiment the model produced harmonic oscillations near $h$, whereas typical relaxation behavior resulted near the bistable region. Qualitatively the same diagram was obtained in the $T/P_{CO}$ parameter plane; here the oscillations occurred in the range of high $T$ and $P_{CO}$.

The bifurcation shown in Fig. 8 is not complete. There must in addition be sn curves emanating from the TB points; also the Hopf bifurcation became subcritical at a certain pa-

![Figure 9](https://example.com/figure9.png)

### FIG. 9. Complete bifurcation set of the reconstruction model (4a)-(4c), not drawn to scale in order to visualize all different regions (whose phase portraits are depicted in the lower part of the figure); see Table I for the notation.

![Figure 10](https://example.com/figure10.png)

### FIG. 10. (a) Skeleton bifurcation set in the $P_{CO}/P_{CO}$ parameter plane at 525 K. Full (dashed) lines denote saddle-node (Hopf) curves. There is an additional very narrow bistable region denoted $A$ at low pressures, which is not present at 540 K (Fig. 8). (b) Bifurcation diagram as in (a), but here the stationary state CO coverage $u$ is plotted vs $P_{CO}$ for those values of $P_{CO}$ at which Hopf (dashed) and sn bifurcations (full lines) occur. This type of diagram (where a phase variable is plotted vs a parameter) was chosen in order to make all regions clearly visible, in particular the new bistable one $A$.
parameter combination (which requires a DH and an snp curve). This fine structure occurred, however, in such narrow parameter intervals that it would hardly be discernible on the scale used in Fig. 8. Therefore an exploded view of the complete bifurcation diagram is reproduced in Fig. 9 (not drawn to scale). The sl curves end on SNL's on the opposite sn branch; these also bound the sniper bifurcation. A stable limit cycle exists up to the degenerate Hopf bifurcation DH (cf. Figs. 8 and 9). Note that the diagram is organized by five different codimension-2 bifurcations. Not surprisingly only the skeleton diagram (Fig. 8) was observed experimentally, while the detailed fine structure in Fig. 9 has escaped detection.

For lower temperatures additional features were obtained in the 2-parameter bifurcation sets. At 525 K another small bistable region had appeared interrupting the h line (with two more TB points), see Fig. 10. This region grew for lower T so that the two bistable areas overlapped (Fig. 11, 520 K). Finally, at 490 K the hitherto separate sn curves had merged into one uninterrupted line exhibiting a total of four cusps (Fig. 12). As in Fig. 8, Figs. 10–12 again only show the behavior at low pressures, the additional C and TB at high pressures are not affected by the transitions shown.

The various two-parameter cuts suggest the occurrence of two codimension-3 phenomena, see the schematic representation of the four diagrams corresponding to Figs. 8, 10, 11, and 12 in Figs. 13(a)–13(d). While the transition from (a) to (b) can be understood with a Takens–Bogdanov cusp (TBC) point, a codimension-3 phenomenon which would change the diagram (c) to the one in (d) has to our knowledge not been described yet.

C. Mixed-mode oscillations

For not too high temperature typical mixed-mode oscillations (MMOs) were observed on Pt(110). Since no behavior more complex than a simple limit cycle is predicted from the above model (4a)–(4c), obviously another effect has to be taken into account. Under conditions where MMOs occur, faceting of the surface was observed and its degree shown to vary during oscillations. The oxygen sticking coefficient was found to be significantly enhanced on a faceted surface.
FIG. 13. Schematic drawing of the skeleton bifurcation diagrams of Figs. 8, 10, 11, and 12. Codimension-3 bifurcations appear to occur between (a) and (b), as well as between (c) and (d). The saddle-node curves between the TB points (---) involve an unstable, the other (---) a stable node.

The degree of faceting $z$ is a consequence of a competition between the formation of facets (with the free energy of the reaction as driving force) and thermal annealing (the flat surface is thermodynamically favored),

$$z = k_f u' v' w(1 - z) - k_z (1 - u).$$  \quad (4d)

The facets were found to develop from a predominantly CO-covered state (after the reconstruction was lifted), but only as long as there was noticeable turnover. In a crude approximation this can be modeled by setting their formation proportional to the reaction rate $(u' v)$ on the $1 \times 1$ structure $(w)$. The term $(1 - z)$ introduces a maximum degree of faceting. $k_f$ can to a first approximation be assumed to be independent of temperature.\(^{49,52}\)

The reordering process is, in contrast, strongly temperature dependent and slowed down by high CO coverage, which is why the term $(1 - u)$ was introduced. The rates $k_f$ and $k_z$ (as well as the activation energy for the latter) were estimated from the rate at which facets form and the temperature dependence of the saturation level\(^{49,52}\) (see data cited in Sec. III and Table II). The increase of oxygen sticking probability due to faceting was accounted for by adding a term $s_{03} z$ to $s_0$ in (4b), i.e.,

$$s_0 = s_{01} w + s_{02} (1 - w) + s_{03} z.$$

The stationary degree of faceting and the reaction rate were computed from the full model (4a)-(4d) and are reproduced in Fig. 14 as a function of $p_{CO}$. The resulting curve is in reasonable agreement with the experimental ones,\(^{49}\) although in the model the decrease towards high $p_{CO}$ is considerably flatter than in experiment. This is, however, probably due to the fact that in this region the facets develop extreme slowly so that in the experiments the saturation may not have been reached.

Mixed-mode oscillations in the four-variable model (4a)-(4d) were found via direct integration (Fig. 15, to-

FIG. 14. Stationary state reaction rate and degree of faceting calculated from the four-variable model (4a)-(4d) as a function of $p_{CO}$. Full line: reaction rate without faceting $(k_f = 0)$; dotted line: reaction rate with facets; dashed line: degree of faceting $(p_{CO} = 1.2 \times 10^{-4} \text{ mbar, } T = 540 \text{ K})$.

FIG. 15. Experimental (a) and (b) and calculated (c) mixed-mode oscillations (a) $p_{CO} = 7 \times 10^{-4} \text{ mbar, } T = 540 \text{ K, } p_{CO} = 2.1 \times 10^{-4} \text{ mbar; }$ (b) $p_{CO} = 4.4 \times 10^{-4} \text{ mbar, } T = 541 \text{ K, } p_{CO} = 1.8 \times 10^{-4} \text{ mbar; }$ (c) $p_{CO} = 1.2 \times 10^{-3} \text{ mbar, } T = 540 \text{ K, } p_{CO} = 4.2 \times 10^{-5} \text{ mbar}. $
gether with experimental examples). As can be seen from the time series in Fig. 15(c), there are small oscillations on a mainly O-covered surface. During these oscillations, when it drops below a critical value the system jumps to a predominantly CO-covered state, on which facets develop again. The existence region of the MMOs is located between those of typical harmonic (near h) and relaxation behavior (Fig. 16).

The occurrence of MMOs can be rationalized using a slow manifold approach, i.e., using the slowest variable z as a parameter and solving for the limit sets of the others as a function of z. We obtained a Hopf bifurcation of the fast subsystem for decreasing z followed by a sharp rise in amplitude, around which MMOs occur when z drifts back and forth for high O resp. CO coverage (see Ref. 59 for details).

Time series as in Fig. 15(a), i.e., square-wave forms with small superimposed oscillations both on the high and low Δφ level were not obtained in the model.

V. DISCUSSION

The three-variable model (4a)-(4c) (reconstruction model of surface oscillations) does not only predict those types of bifurcations observed in experiment, but also quantitative aspects such as the location of the bifurcations in parameter space as well as the oscillation periods and amplitudes are in very good agreement with the experimental data at high temperature (respectively, low pressure). However, the oscillatory region does not reach down to low temperatures, in contrast to experiment.5,6 This could be remedied by introducing a “defect term” in oxygen adsorption [as was necessary in a certain model for Pt(100) in order to find oscillations at all]5, i.e., assuming that for some fraction of the surface there is no inhibition by preadsorbed CO. Recently, direct experimental evidence for small patches of the surface with enhanced oxygen adsorption [even on a carefully prepared Pt(110) single crystal surface] was found in measurements with high spatial resolution (<1 μm) using photoemission electron microscopy (PEEM).1,12 On a predominantly CO-covered surface with stationary overall reaction rate target patterns were observed to emanate from oscillating centers (presumably defects) which were still discernible when moving into the oscillatory region by lowering PO. Nevertheless, the introduction of an overall “defect term” into Eq. (4b) seems somewhat ambiguous, and it is very hard to quantify. Such defects will naturally have to be included when modeling the mentioned target patterns in future work using partial differential equations (PDEs) which may then also result in a better fit of the oscillatory region at low temperature. On the other hand, it is by no means clear whether the low-T oscillations are really defect related. A refinement of the phase transition kinetics (e.g., a coverage dependence of kₙ) may also have the desired effect.

Faceting of the Pt(110) surface is connected with the formation of regular microscopic structures.67,50 However, the model (4a)-(4d) only accounts for the average change of oxygen sticking probability neglecting not only the form of the facets, but also spatial variations, which certainly constitutes an oversimplification. Thus, from the variety of experimentally observed MMOs (Refs. 3, 7, and 8) only a certain type could be described (Fig. 15). While the four-variable model demonstrates qualitatively that faceting can lead to mixed-mode behavior, a realistic model would probably have to include spatial variations (cf. Ref. 51).

**FIG. 16.** Top: existence region (II) of mixed-mode oscillations between the region of harmonic (I) and relaxation oscillations (III) (P₉₃ = 4.2×10⁻³ mbar, T = 540 K). Bottom: typical time series from the various regions; P₀ = 1.22 (a), 1.21 (b), and 1.20×10⁻⁴ mbar (c).
In Sec. IV it was demonstrated how a model can be developed stepwise in order to comprise increasingly complex dynamics by including a minimum number of variables and just those which are essential for a given type of behavior. With the present system bistability, oscillations and MMOs were obtained with 2, 3 resp. 4 variables. Such a stepwise procedure does not only simplify the development of a model, but also gives insight into the question where a certain dynamic behavior stems from and which effects do not cause qualitatively different features, but only lead to quantitative corrections (such as the coverage dependence of CO desorption, Sec. IV A). The model was, at first, kept as simple as possible, i.e., only the minimum number of effects to produce a given behavior were included. In our opinion, it does, in general, not make much sense to study even simpler models which, as a consequence of the negligence of still more effects, predict unphysical qualitative features (such as unrealistic states or a nongeneric bifurcation structure, cf. Ref. 57). With the present system, such problems arise if CO desorption or the asymmetric inhibition of adsorption are not taken into account (Sec. IV A). There exist quite a few studies of models for CO oxidation which are oversimplified in the above sense, both in Monte Carlo simulations and using mean field theory. Although such models can reveal phenomena which are interesting per se, it should not be claimed that they can be regarded to represent any realistic chemical reaction scheme.

It is, of course, not difficult to do realistic simulations also with a Monte Carlo technique. Such an approach can also model surface oscillations, if the phase transition and its effect on oxygen adsorption is included or if an attractive interaction between adsorbed species is introduced. The good agreement of the present model with experiment suggests, however, that in contrast to the claim made in oscillations on a surface can indeed be successfully modeled with ordinary differential equations.

Although bistability can theoretically be embedded in a one-dimensional phase space, chemical systems generally do not allow this phenomenon in a single species, since competition between different processes is required, which can usually only be achieved with several species in a chemically realistic way. In the present model, two species were required for bistability. One of these, namely, \( v \), changes considerably faster than the other (\( u \)) so that it can, to a reasonable approximation, be eliminated adiabatically. This means that the basic LH model (4a) and (4b) represents effectively a one-variable system. It becomes unstable because the adsorption kinetics are of different order for \( O_2 \) and CO, that is to say, the instability is robust with respect to the kinetic order of the surface reaction (3c), whereas different orders for (3a) and (3b) are crucial for bistability. Inclusion of the phase transition (4c) introduces a negative feedback loop (\( CO_{ad} \) causes a structural change, which enhances oxygen adsorption, in turn lowering the CO coverage by reactive removal) on a longer time scale because the phase transition is the slowest process in Eqs. (4a)–(4c). Such an effect generally leads to oscillations in a system bistable without it. The type of negative feedback introduced by faceting is closely related (facets form on a CO-covered surface and lead to enhanced oxygen adsorption), but (presumably due to the high mass transport of Pt required) it occurs on a still significantly slower time scale. It is just the combination of two negative feedbacks occurring on different time scales which gives rise to mixed-mode oscillations.

The period-doubling cascade to chaos and the subsequent transition to hyperchaos found experimentally at high \( T \) when lowering \( p_{CO} \) starting near a predominantly CO-covered surface cannot be explained from the ODE system described in Sec. IV. Faceting is almost certainly not involved in the occurrence of chaos, since facets were only observable for lower temperature, whereas at high \( T \) (where chaos was obtained) the surface remained essentially flat. Actually we did get a pd cascade in a five-variable model, in which we kept track of the coverages of CO and O on the two surface structures separately, i.e., the five variables were CO and O, each on the 1 \( \times \) 1 and 1 \( \times \) 2 phase (\( u_1, u_2, v_1, v_2 \)) as well as the 1 \( \times \) 1 coverage \( w, z \) was not included. This model is, however, unsatisfactory because it needs to contain arbitrary parameters (e.g., the rate constants for cross-reaction terms such as CO \( 1X2 + O 1X1 \)) which are up to now not accessible experimentally. Moreover, chaos was in the computations only obtained for unrealistic values of those parameters which are fairly accurately known from experiment. Vishnevskii and Savchenko found three different adsorbed oxygen species on Pt(110) using TDS and XPS, inclusion of which may also lead to chaos in model calculations. However, these studies were done under conditions where facet formation is strong, while it is unclear whether different states of \( O_{ad} \) also exist on a flat surface. Therefore, such an interpretation of the occurrence of chaos remains highly speculative. Moreover, a model with different \( O_{ad} \) species would again require parameters arbitrary to some extent, since the differences in reactivity of the various species can only be guessed for the time being.

On the other hand, recent PEEM measurements suggest that efforts to model chaos in the CO oxidation on Pt(110) with ODEs may be futile. At the highest temperatures at which oscillations were still observable, only time-periodic oscillations resulted and no spatial structures were observed—a situation which can clearly be modeled with ODEs. In contrast, whenever a transition to chaos occurred, the period-1 oscillations near the CO-covered state already consisted of ordered (but inhomogeneous) spatial structures (in the form of standing waves, mostly as stripes perpendicular to the [1 10] direction) which oscillated strictly in phase over the whole surface. There is some evidence that the first period doubling is still associated with an ordered spatial pattern, whereas upon further reduction of \( p_{CO} \) (i.e., when the integral time series became chaotic) turbulent-like moving spatial patterns resulted. These observations suggest that chaos in the system studied occurs as a consequence of a partial breakdown of spatial correlation, which cannot be described with ordinary differential equations of the form presented in Sec. IV. Moreover, in an ODE system, one would probably have to postulate yet another effect (such as yet another differently bound adsorbed species) in order to explain the occurrence of hyperchaos. In
contrast, a chaotic hierarchy of patterns may become a natural consequence in a spatiotemporal model, in which—upon change of a control parameter—the spatial order breaks down more and more. Modeling of such effects, which will need solution of partial differential equations, will be the subject of future work.

VI. CONCLUSION

Bistability and simple oscillations in the CO oxidation on a Pt(110) surface can be modeled almost quantitatively with a simple system of ordinary differential equations. Mixed-mode oscillations can be qualitatively understood by an extension of this model. A successful quantitative description of the experimentally obtained mixed-mode behavior and transition to chaos will most likely require to take spatial effects into account.

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