

Conditions for the Occurrence of Kinetic Oscillations in the Catalytic Oxidation of CO on a Pt(100) Surface

By M. Eiswirth, R. Schwankner and G. Ertl

Institut für Physikalische Chemie, Universität München, Federal Republic of Germany

In memoriam Georg-Maria Schwab

(Received June 3, 1985)

Catalysis / Kinetic oscillations / Synergetics

The rate of catalytic CO oxidation at low pressures ($< 10^{-3}$ Torr) on a well-defined Pt(100) single crystal surface may exhibit sustained temporal oscillations which can conveniently be followed by means of the variation of the work function. In the present work the conditions (p_{O_2} , p_{CO}) at $T = 480$ K, as well as (p_{CO} , T) at $p_{O_2} = 2 \times 10^{-4}$ Torr for the occurrence of oscillations were experimentally established. The results agree qualitatively well with the predictions of a recent theoretical model based on the periodic transformation of the surface structure.

Die Geschwindigkeit der katalytischen CO-Oxidation bei kleinen Drucken ($< 10^{-3}$ Torr) an einer wohldefinierten Pt(100)-Einkristall-Oberfläche kann zeitliche Oszillationen aufweisen, die anhand der Variation der Austrittsarbeit verfolgt werden können. In der vorliegenden Arbeit wurden die Bedingungen (p_{O_2} , p_{CO}) bei $T = 480$ K, sowie (p_{CO} , T) bei $p_{O_2} = 2 \times 10^{-4}$ Torr für das Auftreten der Oszillationen experimentell bestimmt. Die Ergebnisse stehen qualitativ in guter Übereinstimmung mit den Vorhersagen eines kürzlich entwickelten theoretischen Modells, das auf einer periodischen Umwandlung der Oberflächenstruktur beruht.

1. Introduction

After the discovery of sustained temporal oscillations in the rate of catalytic CO oxidation over supported Pt catalysts in the atmospheric pressure regime by Wicke's group [1] considerable attention has been paid to the study of these phenomena [2]. The occurrence of such oscillations even at well-defined single crystal surfaces at low pressures ($\sim 10^{-4}$ Torr) was first reported in 1982 [3] and was recently also confirmed by other groups [4, 5].

It turned out that these oscillations were most pronounced with the Pt(100) surface which may exist in two structural modifications with quite different adsorptive properties: A reconstructed hexagonal arrangement of the surface atoms (hex) which transforms into the non-reconstructed 1×1 -configuration if the coverage of adsorbed particles exceeds a critical value. This structural transformation can be observed by low energy electron diffraction (LEED), and application of this technique demonstrated that the kinetic oscillations are associated with periodic changes of the surface structure between these two phases [6]. By scanning the electron beam used for LEED over the single crystal surface it was possible to show that spatial self-organisation of the oscillations is accomplished by a wave-like propagation of the structural transformation across the macroscopic surface area [7]. The elementary processes underlying these effects could be successfully modelled theoretically by the solution of a set of coupled differential equations which were established on the basis of the independently studied adsorption, desorption and surface reaction steps of the particles involved [7, 8]. This theoretical work [8] also predicted a diagram $f(p_{\text{CO}}, p_{\text{O}_2})$ for the existence of the oscillations at a fixed temperature ($T = 480 \text{ K}$). Such an existence diagram was experimentally determined in the present work together with conditions p_{CO} , T at fixed oxygen partial pressure. Stability of gas pressure and purity revealed to be crucial for these type of experiments. For this purpose a new gas inlet system was developed which provided much better reproducibility and will be described in some detail.

2. Experimental

The experiments were performed under continuous-flow conditions in an UHV system pumped by a turbomolecular pump which was equipped with facilities for LEED, Auger electron spectroscopy (AES), as well as with a quadrupole mass spectrometer and a Kelvin probe for continuously recording the variation of the work function $\Delta\phi$ [9]. The latter quantity had been found to parallel directly the variation of the reaction rate [3, 6] and was therefore used as a convenient monitor for the kinetic oscillations.

$\Delta\phi$ -signal was recorded by a chart recorder, respectively fitted to a microcomputer (Commodore 8296D) via a digital multimeter (Keithley 195a). For starting the oscillations the desired temperature and O_2 -pressure were adjusted and then the CO -pressure increased steplike. If the oscillations did not start in this way the sample was briefly annealed and/or the CO pressure continuously decreased again. Usually the oscillations were allowed to stabilize for about one hour which made the total experiments rather tedious.

The reactants were introduced into the UHV chamber through bakeable leak valves. The feedback-stabilized flow control system is shown schematically in Fig. 1. It consists of a capacitive pressure transducer (MKS Baratron 222 BHS), a controller unit (MKS 250 B) and a tunable magnetic valve (MKS 248 A) for each of the two feed lines in order to keep the pressures at the high-pressure sides of the leak valves constant to within $1^0/00$ at values of around 40 Torr. This gas inlet system could be baked out and evacuated independently from the UHV chamber. The two gas lines could be operated separately

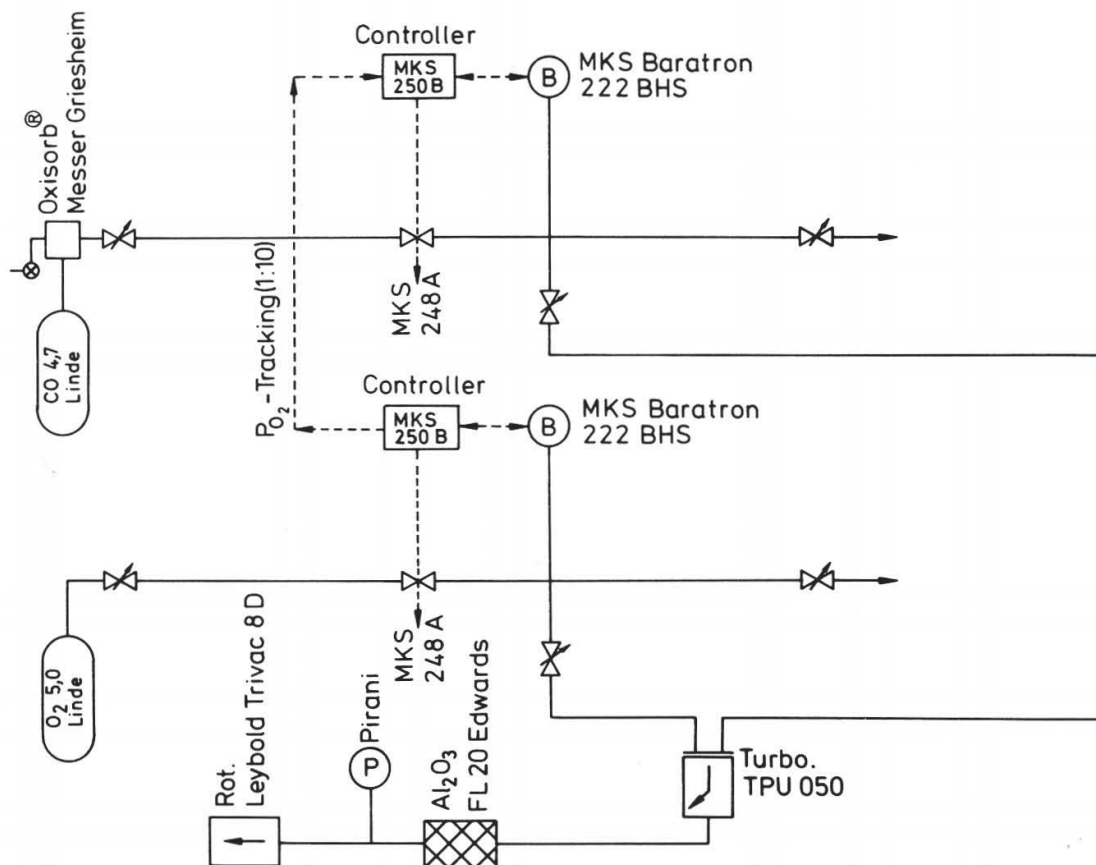


Fig. 1. Schematic diagram of the feedback-controlled gas inlet system

or in a tracking mode, whereby the pressure *ratio* was kept constant by interconnecting the two controller units. The desired partial pressures inside the UHV chamber were first roughly adjusted by opening the leak valves; their exact control was then achieved by the setting of the feedback system on the controller units. The latter could also be driven by an external ramp or frequency generator, thus enabling periodic modulation of the pressure for studying forced oscillations [11]. The pressures in the UHV recipient were continuously measured by an ionization gauge (Varian) without further correction.

The Pt(100) surface contained initially traces of Ca and Si impurities as monitored by AES which were removed by repeated Ar^+ ion sputtering at 800 K sample temperature followed by cycled heating to 900 K in 10^{-4} Torr O_2 as well as in UHV. The latter procedure was also applied for 30 min before and after each experiment. The sample temperature was determined to within 0.2 K by a chromel-alumel thermocouple spot-welded to the center rear. Possible inhomogeneities of the temperature across the surface during the oscillations could be excluded on the basis of IR emission photographs taken through a CaF_2 window.

Gases with the highest commercially available purities were used (O_2 : Linde 0.5; CO: Linde 4.7). Although for CO no impurities could be detected by the quadrupole mass spectrometer, further purification over Oxisorb[®] prior to inlet into the UHV chamber turned out to be a necessary prerequisite for establishing sustained oscillations. Oxisorb[®] consists of a molecular sieve and a coordinatively unsaturated Cr(II) compound on a carefully dried silicagel support and removes trace amounts of O_2 , halogens, H_2O , NO_x , H_2S , SO_2 and unsaturated hydrocarbons by reduction, chemisorption and polymerization, respectively [10]. Since the oscillations were very sensitively influenced

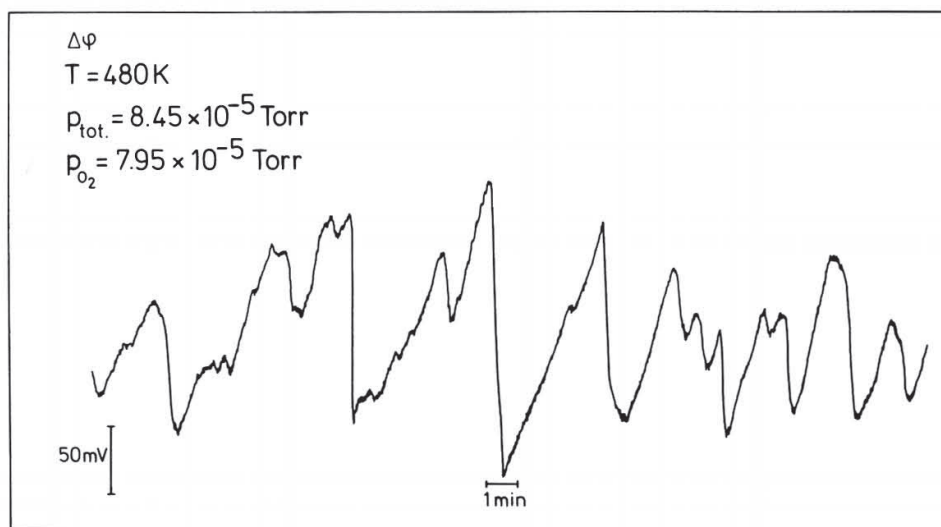


Fig. 2. A typical example for irregular oscillations

by hydrocarbons and water, additional precautions were taken in order to suppress gas contamination by the pumping devices of both the UHV chamber and the gas inlet system. The best results were obtained by mounting large bakeable traps between rotation and turbomolecular pumps which were filled with alternate layers of activated alumina (Edwards H026-00-050) and zeolithe (Pfeiffer PK 001-187-T) which had to be replaced once in three months.

It turned out that purposely added hydrogen had also a significant effect on the oscillations: Already 0.01% H₂ affected the amplitudes and frequency behaviour markedly, and the addition of 2% H₂ to the gas flow suppressed the oscillations completely. The influence of traces of hydrocarbons (C₂H₄) was even more drastic.

3. Results

Once the oscillations were established they could be maintained for up to 30 h when they were purposely terminated.

Recent experiments near atmospheric pressure [5] revealed the formation of a stable and rather unreactive surface oxide after prolonged reaction, and the formation and slow reduction of such an oxide species was underlying a previous model for a theoretical treatment of the oscillations [12]. Under the present low-pressure conditions ($< 10^{-3}$ Torr) no indication of the formation of such an oxide species was found. After 30 h reaction and subsequent brief flashing to 900 K (removal of chemisorbed oxygen) the Auger spectrum was characteristic for a clean surface and showed no detectable oxide formation.

Two typical examples for kinetic oscillations as monitored through the work function change $\Delta\phi$ are reproduced in Figs. 2 and 3. In most cases these were irregular as in Fig. 2. Regular oscillations as in Fig. 3 were restricted to situations where the CO coverage was high and occurred

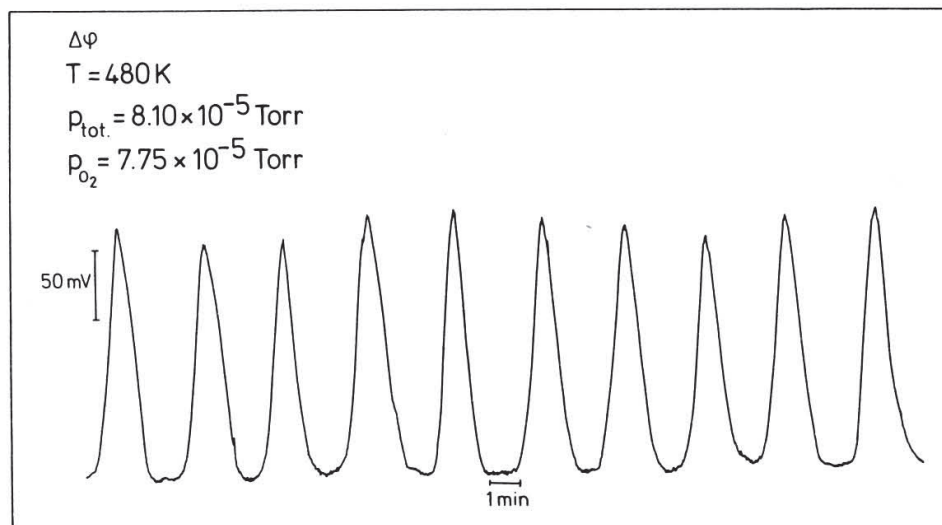


Fig. 3. A typical example for regular oscillations

predominantly at high total pressures (near 10^{-3} Torr). In these cases the $\Delta\phi$ -amplitudes reached values of up to 350 meV, while otherwise the amplitudes were typically around 250 meV.

In the theoretical treatment mentioned above [8] the conditions for the occurrence of oscillations were determined as a function of the oxygen and CO partial pressures at a fixed temperature of 480 K. For this reason corresponding experiments were performed at 480 K and at fixed p_{O_2} while p_{CO} was stepwise varied. In this way the existence region for the oscillations as reproduced in Fig. 4 was determined. Fig. 5 shows the low pressure range on an enlarged scale. Each boundary was determined repeatedly in both directions, i.e. either by increasing or decreasing the CO pressure. While the error bars for p_{O_2} are negligibly small, an inaccuracy in p_{CO} arose from the fact that p_{CO} was usually much smaller than p_{O_2} and only the total pressure ($p_{O_2} + p_{CO}$) was recorded by the ionisation gauge.

In region A (low p_{CO}) the work function remained on a constant high level indicating an excess of adsorbed oxygen on the surface. Conversely in region B the work function was constant and low which reflects a high CO coverage.

With decreasing total pressure the oscillatory region becomes increasingly narrower. Below a critical $p_{O_2} = 2.8 \times 10^{-5}$ Torr (at 480 K) oscillations were no longer detectable. An increase of p_{CO} in this range leads to direct switching from the O- to the CO-covered surface.

These conclusions were confirmed by additional LEED observations: Region A is characterized by the 'complex' pattern of adsorbed oxygen [13], in region B the $c2 \times 2$ -CO LEED pattern [14] is visible, while near the low pressure 'triple point' the LEED pattern consists of a superposition of spots from the hex and the $c2 \times 2$ -CO phase. In the oscillatory region

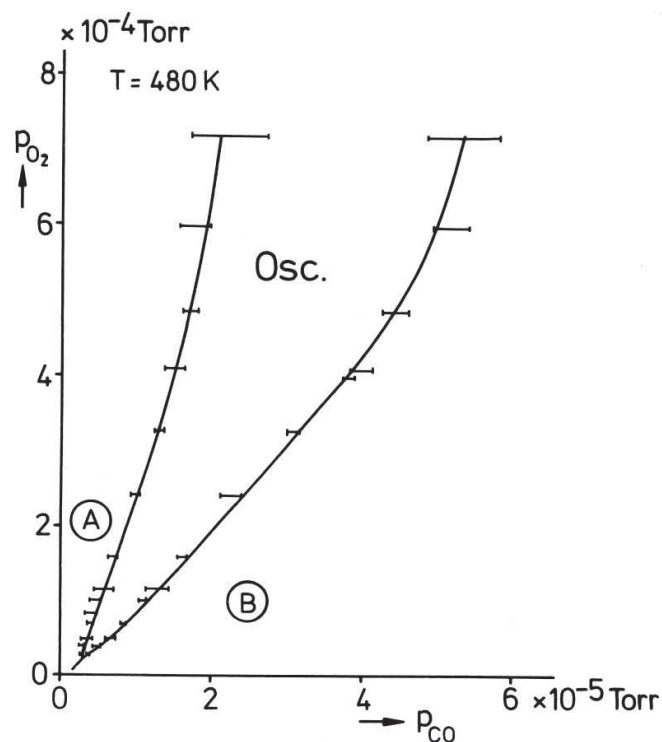


Fig. 4. Existence region (p_{O_2} , p_{CO}) for the oscillations at $T = 480 \text{ K}$

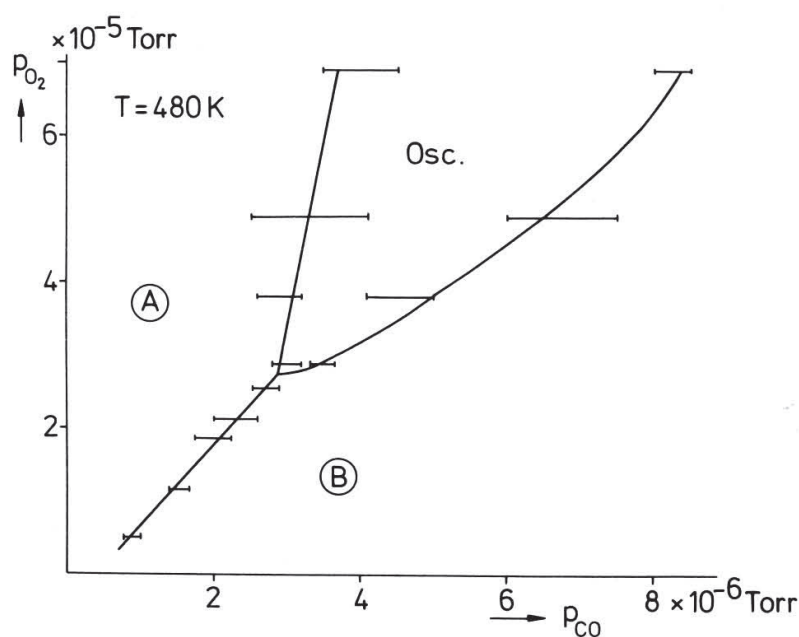


Fig. 5. The low pressure range of Fig. 4 with enlarged scales

the surface structure changes periodically between hex and $c2 \times 2\text{-CO}$, as observed previously [6, 7].

In a different set of experiments the conditions for oscillations were explored as a function of p_{CO} and T at a constant $p_{\text{O}_2} = 2 \times 10^{-4} \text{ Torr}$.

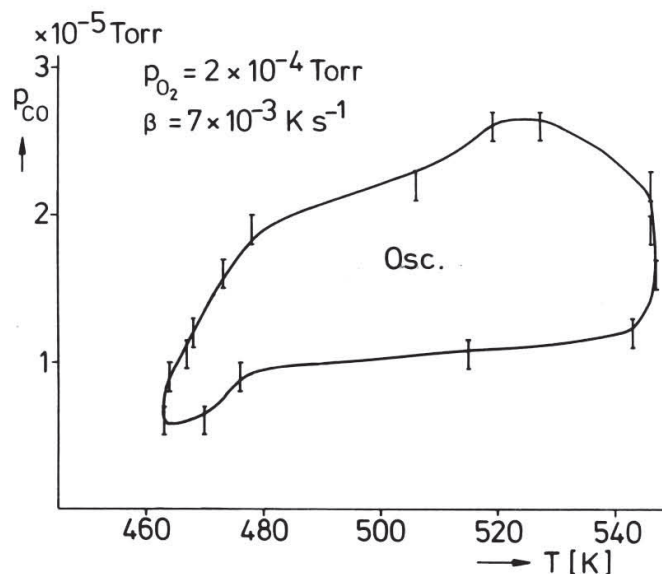


Fig. 6. Existence range (p_{CO} , T) for the oscillations at $p_{\text{O}_2} = 2 \times 10^{-4}$ Torr. The heating rate was $\beta = 7 \times 10^{-3} \text{ K s}^{-1}$

Now a certain CO pressure was established at low enough temperature and then the temperature was very slowly increased at a rate of 0.007 K/s and the onset and dying of oscillations was recorded. The results are reproduced in Fig. 6 and demonstrate that in this case the oscillations are restricted to a closed range of p_{CO} and T . The boundaries with respect to p_{CO} correspond to the data of Fig. 4 at a given p_{O_2} (and T). The existence of a limited temperature range over which (for fixed p_{O_2} and variable p_{CO}) oscillations occur had already been established in Ref. [3].

4. Discussion

The single steps underlying the oscillations were already elucidated in previous publications [3, 6–8]. Catalytic CO oxidation proceeds via a Langmuir-Hinshelwood mechanism where adsorbed CO reacts with dissociatively chemisorbed oxygen [15]. The Pt(100) surface exists in two modifications, hex and 1×1 , which differ considerably with respect to their adsorptive properties. The clean hex surface is energetically more stable, but transforms into the 1×1 -phase if a critical coverage of CO(+O) is reached due to the higher heats of adsorption in the latter case. If, on the other hand, the CO coverage on the 1×1 -surface drops below another critical coverage the surface structure transforms back into the hex phase. In addition, the oxygen sticking coefficient on the hex surface is several orders of magnitude lower than on the 1×1 -surface, so that the former exhibits an almost negligible reactivity. The oscillations are thus closely linked to the $\text{hex} \rightleftharpoons 1 \times 1$ phase transformations which occur periodically if the local

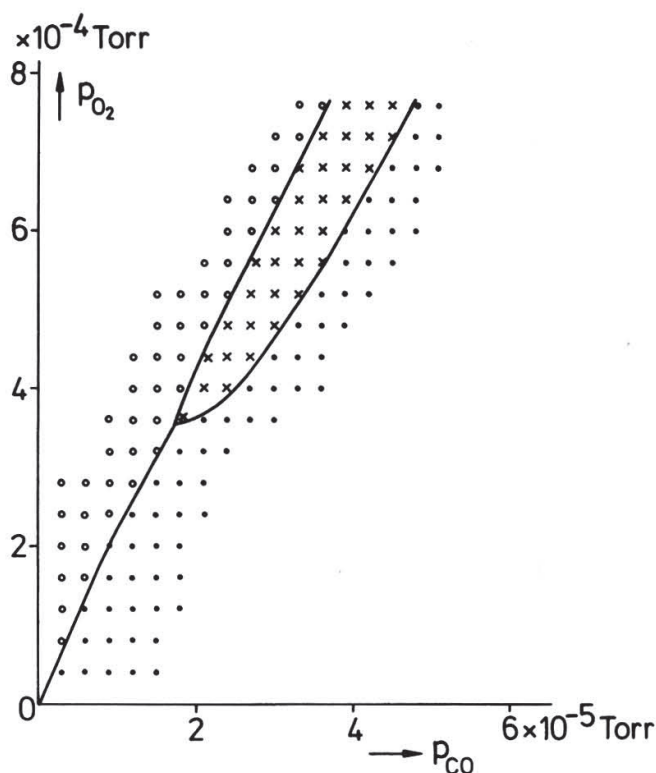


Fig. 7. Theoretical existence region for the oscillations (crosses) after Ref. [8]

CO coverage on the 1×1 -surface in the absence of O_2 is near $\theta_{CO} = 0.5$ [3]. The limited temperature range for the occurrence of oscillations as shown in Fig. 6 can thus qualitatively easily be explained: Below 460 K the steady-state CO coverage is too high and inhibits oxygen adsorption, so that the coverage never drops below the limit for the $1 \times 1 \rightarrow \text{hex}$ transformation. Above 540 K, on the other hand, θ_{CO} is too low and the conditions for the $\text{hex} \rightarrow 1 \times 1$ transformation can never be reached.

For a quantitative treatment of the outlined mechanism a set of coupled differential equations was formulated and solved numerically [8]. Spatial self-organization was achieved by inclusion of a term describing surface diffusion of adsorbed CO. As a consequence a wave-like propagation of the structural transformations across the surface resulted which was verified in recent scanning LEED experiments [7]. The reaction rate as well as the work function change $\Delta\phi$ result from a summation over all local contributions across the surface. As a consequence the resulting oscillations were found to be frequently irregular (as in Fig. 2), but sometimes also regular (as experimentally verified in Fig. 3) — sensitively depending on the chosen parameters.

In this theoretical treatment also a p_{O_2} , p_{CO} -phase diagram for $T = 480$ K was evaluated which is reproduced in Fig. 7 and should be compared with the experimental data of Figs. 4 and 5. Qualitative agree-

ment becomes clearly evident: The open circles in Fig. 7 mark conditions where the surface is predicted to be predominately covered by oxygen, while in the range of the closed circles CO adsorption prevails. These regions correspond to ranges A and B in Figs. 4 and 5. The crosses in Fig. 7, on the other hand, denote the conditions for which theory predicts the occurrence of oscillations. This range has again a lower limit and opens with increasing pressure. However, the pressures of this theoretical lower limit are roughly one order of magnitude higher than found experimentally, and for a given p_{O_2} oscillations occur over a wider range of p_{CO} than predicted theoretically. It should be mentioned that the parameters used for the theoretical calculations have so far not yet been optimized, so that the agreement between theory and experiment can certainly be considerably improved in future work. The main purpose of the present study was to verify some of the qualitative features of the model which — in our opinion — was achieved rather satisfactorily.

Acknowledgements

The authors gratefully acknowledge the support of M. P. Cox who constructed the gas inlet system and of P. R. Norton who borrowed the Pt(100) sample. Financial support was obtained from the Deutsche Forschungsgemeinschaft (SFB 128), the Stiftung Volkswagenwerk, and the Fonds der Chemischen Industrie.

References

1. a) P. Hugo, Ber. Bunsenges. Phys. Chem. **74** (1970) 121; b) H. Beusch, P. Fieguth and E. Wicke, Chem. Ing. Techn. **44** (1972) 445.
2. Reference to the extensive literature of this effect can e.g. be found in Ref. [8].
3. G. Ertl, P. R. Norton and J. Rüstig, Phys. Rev. Lett. **49** (1982) 177.
4. P. R. Norton, P. E. Bindner, K. Griffiths, T. E. Jackman, A. Davies and J. Rüstig, J. Chem. Phys. **80** (1984) 3859.
5. R. C. Yeates, J. E. Turner, A. J. Gellmann and G. A. Somorjai, Surf. Sci. **149** (1985) 175.
6. M. P. Cox, G. Ertl, R. Imbihl and J. Rüstig, Surf. Sci. **134** (1983) L517.
7. M. P. Cox, G. Ertl and R. Imbihl, Phys. Rev. Lett. **54** (1985) 1725.
8. R. Imbihl, M. P. Cox, G. Ertl, H. Müller, and W. Brenig, J. Chem. Phys. **84** (1985) 1578.
9. G. Ertl and D. Küppers, Ber. Bunsenges. Phys. Chem. **75** (1971) 1017.
10. R. L. Burwell, G. L. Haller, K. C. Taylor and J. F. Read, Adv. Catal. **20** (1969).
11. R. Schwankner, M. Eiswirth and G. Ertl, in preparation.
12. B. C. Sales, J. E. Turner and M. B. Maple, Surf. Sci. **114** (1982) 381.
13. P. R. Norton, K. Griffiths and P. E. Bindner, Surf. Sci. **138** (1984) 125.
14. R. J. Behm, P. A. Thiel, P. R. Norton and G. Ertl, J. Chem. Phys. **78** (1983) 7437; 7448.
15. G. Ertl, in: *Catalysis. Science and Technology* (Eds. J. R. Anderson and M. Boudart), Vol. 4, p. 209. Springer-Verlag (1983).