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# TEMPORAL AND SPATIAL SELF-ORGANISATION IN CATALYSIS AT SINGLE CRYSTAL SURFACES

G. ERTL

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, W-1000 Berlin 33, Germany*

The elementary steps underlying the mechanism of a catalytic reaction are also responsible for its rate under steady-state conditions. In special cases the rate will no longer be stationary, but may become oscillatory or even chaotic. These phenomena have to be ascribed to the nonlinear character of the coupled differential equations modelling the temporal behavior of the surface concentrations of the reacting species. As a consequence, these concentrations may also exhibit spatial differences, even on an *a priori* uniform single crystal surface, leading to spatiotemporal patterns such as propagating and standing waves as well as 'chemical' turbulence. Experimental evidence for these effects is presented for a particular system, the oxidation of CO on a Pt(110) surface.

**Keywords:** Oscillatory catalytic reactions, spatial differences in surface concentrations of reactants, carbon monoxide oxidation on Pt(110)

A catalytic reaction, if operated in a flow reactor under fixed external conditions, such as temperature or flow rates of the reactants, will usually exhibit a constant reaction rate. In special cases, however, this rate may vary with time in a periodic or aperiodic manner. Oscillatory phenomena of this type were first observed with supported catalysts under atmospheric pressure conditions [1], and became recently also the subject of intense research with well-defined single crystal surfaces at low pressures [2]. As an example, fig. 1 shows, for the catalytic oxidation of CO on a Pt(110) surface, the variation of the rate of $CO_2$ formation together with the work function change ($\Delta\phi$) for fixed external conditions [3]. $\Delta\phi$ is essentially proportional to the oxygen coverage, $\Theta_O$ which hence varies in phase with the rate as monitored through the $CO_2$ partial pressure by means of a quadrupole mass spectrometer. As can be seen, the CO partial pressure varies by about 1% through the modulation of the reaction rate, while the relative effect on $p_{O_2}$ is much smaller. It should be noted, that usually the variation of the reaction rate will also be associated with a change in temperature. This effect is, however, completely negligible in the present case: The heat released by the reaction under the applied low pressures is much smaller than the electric power continuously fed into the single crystal sample in order to maintain the preset temperature.

Generally, the rate of a catalytic reaction is determined by its mechanism, that means the sequence of elementary steps involved. For the CO oxidation on

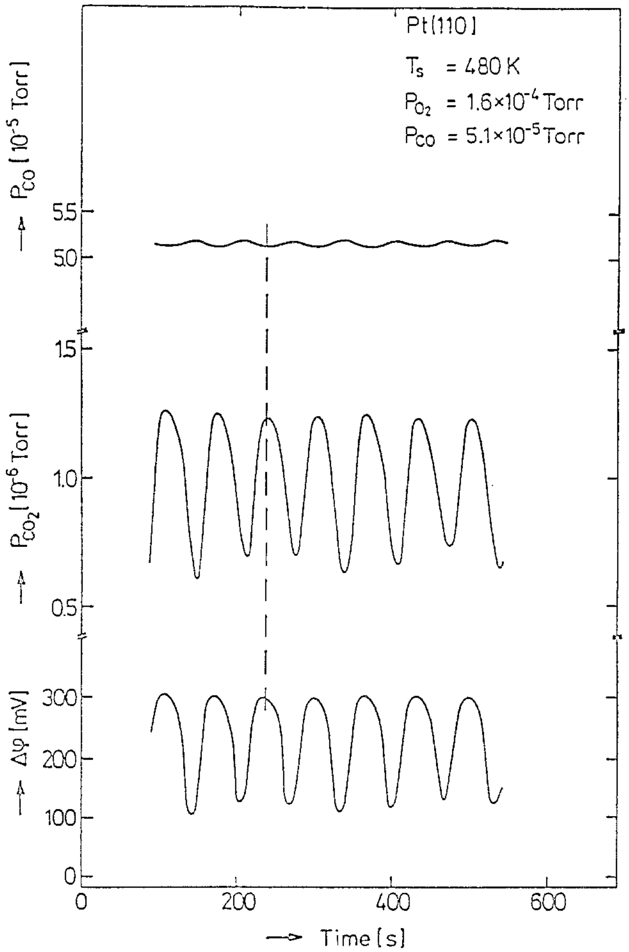
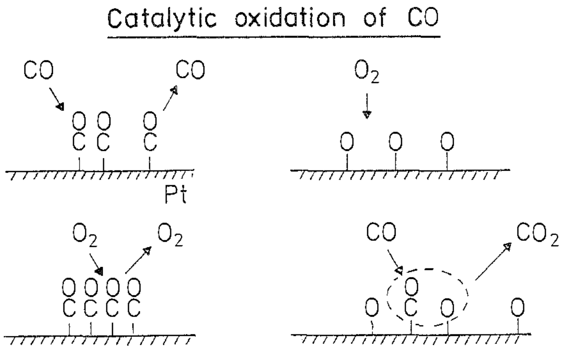


Fig. 1. Kinetic oscillations during catalytic oxidation of CO on a Pt(110) surface [3].

platinum metals the mechanism is well established [4] and is illustrated schematically by fig. 2: CO adsorbs non-dissociatively and has, at the temperatures applied here ( ~ 500 K), also a finite probability for thermal desorption. Oxygen, on the other hand, chemisorbs dissociatively through a molecular precursor and is then so tightly held at the surface that recombinative desorption is to be neglected. The adsorbed CO molecules tend to form densely packed layers which inhibit oxygen adsorption, while the $O_{ad}$ species, on the other hand, form rather open structures which essentially do not block CO adsorption. Formation of $CO_2$ (which is immediately released into the gas phase) proceeds through the Langmuir-Hinshelwood mechanism via recombination of $CO_{ad} + O_{ad}$.

Full quantitative description of these processes comprises, in principle, a system with an almost infinite number of degrees of freedom since about $10^{15}$ particles may be adsorbed on 1 $cm^2$ surface area. This problem is overcome, as



$$\boxed{2CO + O_2 \longrightarrow 2CO_2}$$

$$CO + * \rightleftharpoons CO_{ad}$$
$$O_2 + 2* \rightleftharpoons O_{2,ad} \longrightarrow 2O_{ad}$$
$$O_{ad} + CO_{ad} \longrightarrow CO_2 + 2*$$

$$\frac{d\Theta_{CO}}{dt} = s(CO)\cdot p_{CO} - k_d\Theta_{CO} - k_r\Theta_{CO}\cdot\Theta_O$$

$$\frac{d\Theta_O}{dt} = s(O_2)\cdot p_{O_2} - k_r\Theta_{CO}\cdot\Theta_O$$

$$R = k_r\,\Theta_O\cdot\Theta_{CO}$$

Fig. 2. Mechanism of the catalytic oxidation of CO on platinum (schematic).

generally in chemical kinetics, by applying a continuum model in which the individual particles are replaced by average properties, namely their respective concentrations (in the present case the partial pressures $p_i$ for gaseous species and the coverages $\Theta_i$ for their surface concentrations). By this procedure only very few variables are left and the kinetics may approximately be formulated as indicated in fig. 2. In particular, the reaction rate will be given by $R = k_r\Theta_O \cdot \Theta_{CO}$, while the coverages $\Theta_O$ and $\Theta_{CO}$ are in turn determined by two rate equations which describe the balance between the rates of adsorption, desorption and reaction. The rates of adsorption are governed by the respective sticking coefficients, $s(CO)$ and $s(O_2)$, (normalized with respect to the respective impact frequencies of gaseous particles), which themselves are functions of the coverages. It thus becomes evident that the two variables $\Theta_O$ and $\Theta_{CO}$ are determined by a set of coupled differential equations which are highly nonlinear and depend on the external 'control' parameters $p_{CO}$, $p_{O_2}$ and $T$ (through the rate constants $k_d$ and $k_r$). The solutions of such differential equations may in fact be oscillatory, even if the control parameters are kept constant, – hence the term 'nonlinear dynamics' for phenomena of this type –, and with the present system the oscillatory kinetics may in fact be attributed to the mathematical structure of the underlying equations [5]. More specifically, however, a particular effect has to be taken into account: The kinetic oscillations are confined to conditions for which oxygen adsorption is rate-limiting, and the oxygen sticking coefficient is sensitively affected by the structure of the surface which in turn may be influenced by interaction with the reactants.

The most densely packed Pt(111) surface remains stable under reaction conditions, and no kinetic oscillations are observed with this plane. (Such phenomena may, nevertheless, occur at higher pressures and are then most likely associated with a variation of the chemical state of these surfaces, e.g. by oxide or carbide formation.) Oscillations are, on the other hand, noticed with the more open Pt(100), (110) or (210) planes which undergo structural transformations, either by a variation of the atomic configuration within the surface unit cell (reconstruction) or by the formation of new crystallographic planes (facetting) which effects are both linked to a change of the oxygen sticking coefficient and hence of the reactivity [2].

In the following, we will concentrate on a particular surface, Pt(110), for which so far the most detailed studies have been performed. The clean Pt(110) surface in its stable form is not characterized by an atomic configuration corresponding to its bulk termination (1 × 1-structure) but is reconstructed in a way that every second densely packed row along the [110]-direction is missing (1 × 2-structure) as depicted in fig. 3. The latter phase is obviously energetically more favourable which situation will, however, be altered in the presence of adsorbed CO. The heat of CO adsorption on the 1 × 1-surface exceeds that on the 1 × 2-phase, and hence the surface transforms its structure $1 \times 2 \rightarrow 1 \times 1$, as soon as the CO coverage exceeds a critical value of about $\Theta_{CO} = 0.2$. This process proceeds by local homogeneous nucleation as demonstrated by means of scanning tunneling microscopy [6]. At room temperature local fluctuations of the CO coverage cause breaking of the densely packed [110] rows and small displacements of a few Pt atoms, while at somewhat higher temperatures the displacements of a few Pt atoms, while at somewhat higher temperatures the displacements are of the type illustrated by fig. 4. The 1 × 1-patches from the second atomic layer of the

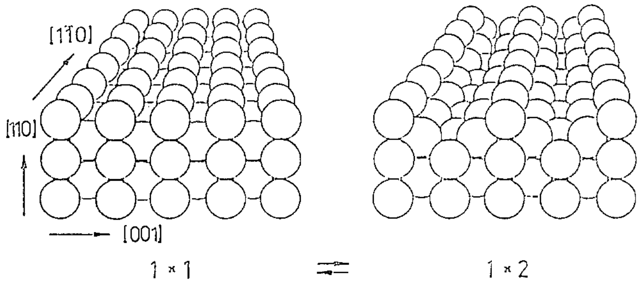


Fig. 3. Structural phases of the Pt(110) surface.

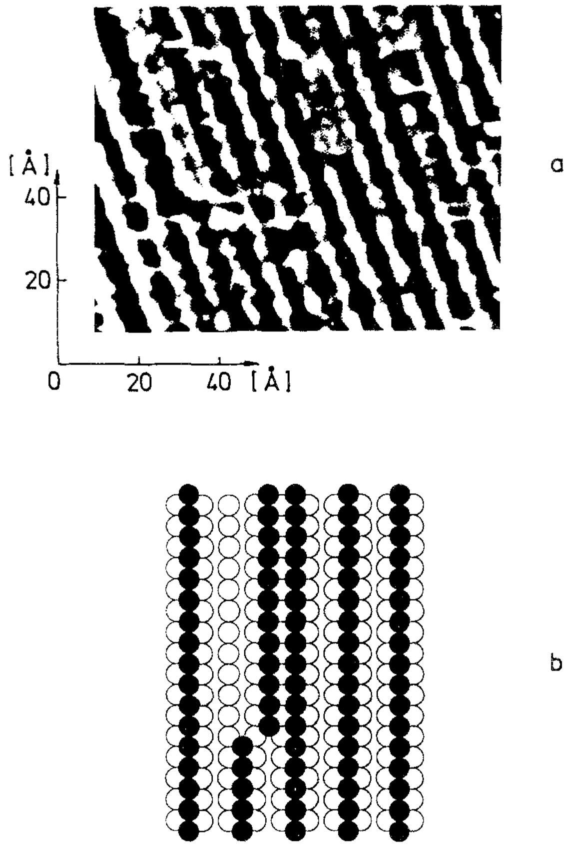


Fig. 4. STM image (a) and ball model (b) of a Pt(110) surface with local lifting of the 1×2-reconstruction by adsorbed CO. $T = 350$ K [6].

substrate exposed in this way to the gas phase exhibit, on the other hand, an increased sticking coefficient for oxygen and in this way the mechanism for a periodic switching of the surface between states of low and high reactivity may be rationalized: Under proper conditions the CO coverage on $1 \times 2$ will become high enough to initiate its transformation into the $1 \times 1$-phase. There the increased rate of oxygen uptake will also cause an enhanced consumption of adsorbed CO by reaction so that the coverage of the latter species drops below its critical value and the surface structure transforms back into the $1 \times 2$-structure where the cycle starts again. Quantitative formulation could be achieved in a mathematical model [7] which explicitely takes into account the dependence of the sticking coefficients $s(\mathrm{CO})$ and $s(\mathrm{O_2})$ on the coverages and (for the latter) on the state of the surface ($1 \times 1$ or $1 \times 2$), which is described by a third differential equation. All the necessary parameters were derived from individual adsorption experiments without any further adjustment, and the solutions of these equations show indeed for particular values of the control parameters ($p_{\mathrm{CO}}$, $p_{\mathrm{O_2}}$, $T$) oscillatory solutions

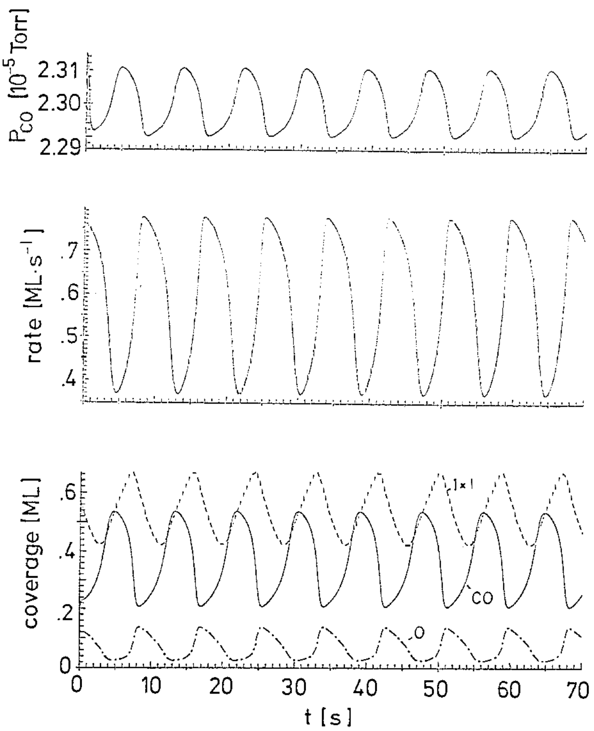


Fig. 5. Theoretical time series resulting from numerical solution of a set of 3 coupled differential equations modelling the kinetics of CO oxidation on Pt(110) [7]. $T = 540$ K, $p_{O_2} = 5 \times 10^{-5}$ mbar, $p_{CO} = 2.3 \times 10^{-5}$ mbar.

of the type shown in fig. 5 in which, for example, $\Theta_O$ and $R$ oscillate in phase as with the experimental data of fig. 1.

Generally, the solutions of the ordinary, nonlinear differential equations of the quoted type will not only exhibit stationary (fixed points) or harmonic oscillatory solutions (limit cycles), but even more complex behavior as is equally verified with the experimental observations. This becomes evident from inspection of fig. 6 which reproduces a time series for the $CO + O_2/Pt(110)$ system recorded at fixed $T$ and $p_{O_2}$ and with stepwise variation of $p_{CO}$ over a rather narrow range from 1.65 to $1.59 \times 10^{-4}$ mbar [8]. At $p_{CO} = 1.65 \times 10^{-4}$ mbar the signal is uniformly periodic, but a qualitative change (= bifurcation) occurs upon slight reduction of this parameter in that now small and large amplitudes are alternating (= period doubling). This behavior continues until at $p_{CO} = 1.60 \times 10^{-4}$ mbar a second period doubling takes place and the time series now becomes composed of sets of four amplitudes with varying height. At $p_{CO} = 1.59 \times 10^{-4}$ mbar the signal is no longer periodic but chaotic, and the whole series represents an experimental verification of the period-doubling or Feigenbaum transition to chaos [9]. In order to illustrate this effect in more detail some of the experimental data of fig. 6 are transformed into phase portraits by the so-called time delay

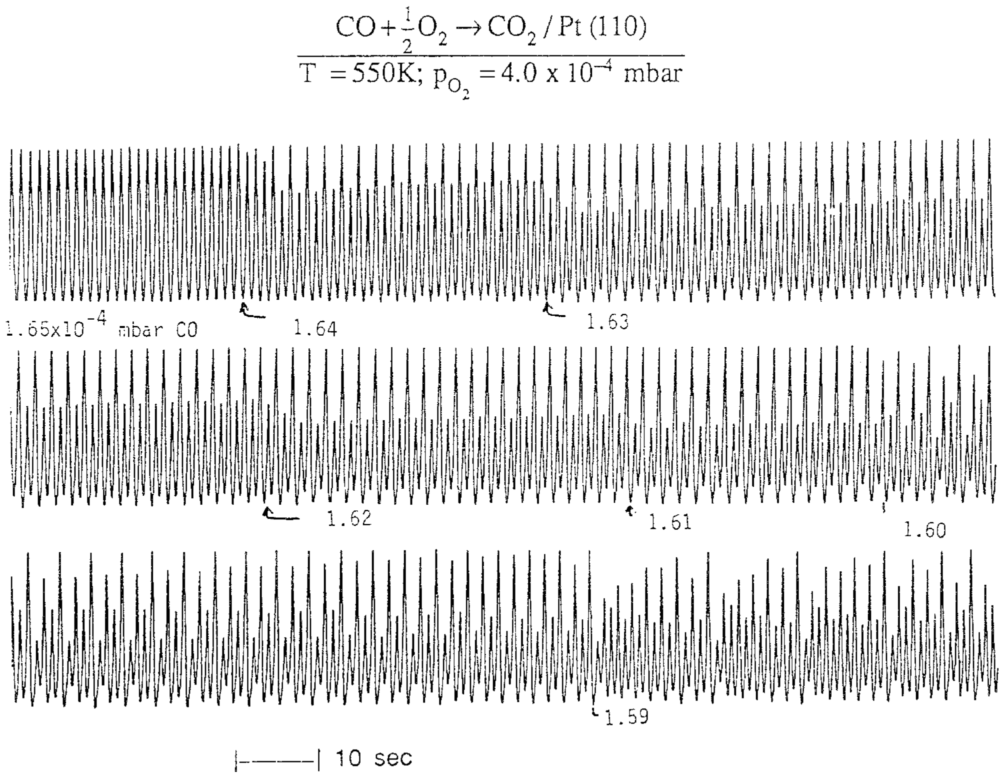


Fig. 6. Time series for the catalytic oxidation of CO on Pt(110) at fixed $T$, $p_{O_2}$ and with stepwise variation of $p_{CO}$, showing the transition from regular harmonic oscillations to chaotic behavior along the Feigenbaum route.

method, according to which the signal $x(t)$ is plotted against $x(t+\tau)$, with $\tau$ being an arbitrary (but fixed) delay time [10]. For $p_{CO} = 1.65 \times 10^{-4}$ mbar a simple closed curve results (fig. 7a) which changes into a double-loop after the first period doubling (b) and into a fourfold loop after the second period doubling (c). The system propagates along these attractors whose widths reflect the variance of the experimental parameters, and up to this stage the future behavior is clearly predictable. This is no longer the case after transition to chaos, for which the 'strange' attractor (d) demonstrates how the temporal evolution even of nearby trajectories diverge.

So far, the modelling of a catalytic reaction involving an almost infinite number of particles in terms of a continuum model, based on the assumption that the state variables (= surface concentrations $x_i$) are only dependent on time, works rather satisfactorily, in that it enables the description of the temporal variation of the reaction rate or of the laterally integrated oxygen coverage such as monitored via work function measurements.

However, it is obvious that observation of temporal variations of such an *integral* property requires some kind of communication between different regions

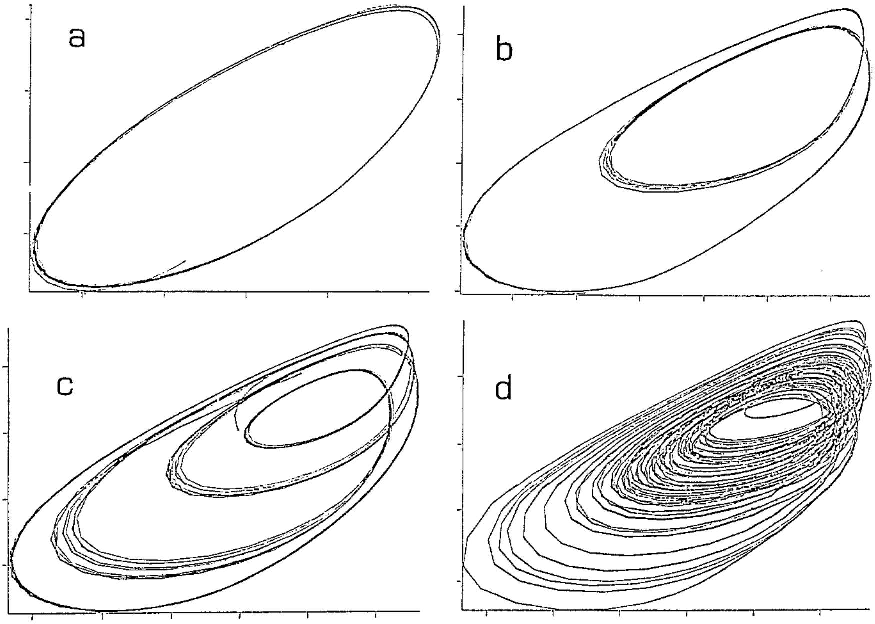


Fig. 7. Phase portraits constructed by the delay time method from the data of fig. 6 for $p_{CO} = 1.65 \times 10^{-4}$ mbar (a), $p_{CO} = 1.63 \times 10^{-4}$ mbar (b), $p_{CO} = 1.60 \times 10^{-4}$ mbar (c), and $p_{CO} = 1.59 \times 10^{-4}$ mbar (d).

of the surface, that means spatial selforganisation. In other words, the state variables $x_i$ are not only functions of time but also of space, $x_i = f(t, \boldsymbol{r})$, and differences in local concentrations will give rise to the occurrence of transport processes. Apart from surface diffusion of adsorbed particles coupled with ongoing reaction, local differences in reactivity might give rise to temperature differences which then lead to communication between various parts through heat conductance. While this latter mechanism plays an important role with supported catalysts at atmospheric pressure conditions, it is certainly negligible for the low-pressure, single crystal systems under discussion here. Finally, the very small variations of the partial pressures of the reactants associated with varying reactivity (cf. fig. 1) may give rise to a practically instantaneous ($\sim 10^{-4}$ s) synchronisation mechanism mediated through the gas phase.

Spatio-temporal pattern formation associated with an oscillatory reaction is, for example, readily observed with the famous Belousov-Zhabotinskii reaction in homogeneous solution [11], where concentration differences of the various species involved are connected with changes in color. In the present case a more refined technique is needed in order to monitor laterally (and temporarily) varying surface concentrations of the adsorbed species. Such differences manifest themselves, for example, by changes of the work function which is highest for the $O_{ad}$-covered surface and lower if it is covered by CO. If a surface is irradiated by UV photons the yield of emitted electrons will be the higher the lower the work

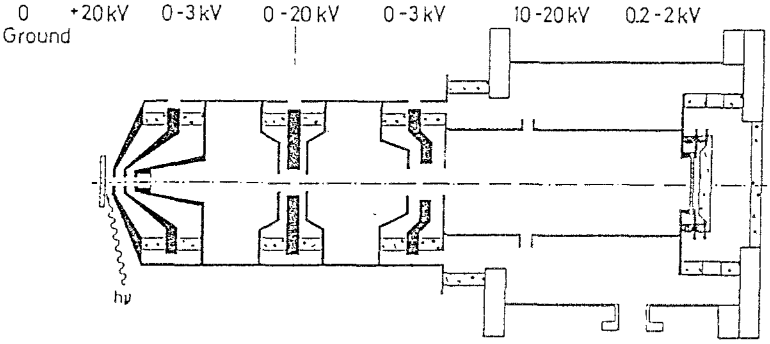


Fig. 8. Principle of the photoemission electron microscope (PEEM) applied for recording the formation of spatio-temporal patterns [12].

function, and combination of this effect with lateral resolution enabled indeed imaging of the spatial formation under discussion here. This goal was achieved by application of a newly developed photoemission electron microscope (PEEM) [12] as illustrated schematically in fig. 8. The sample surface (left) is irradiated by UV light from a deuterium lamp, and the photoemitted electrons are imaged through a system of electrostatic lenses onto a channelplate from where their intensity distribution is transformed onto the greyscale of a fluorescence screen. The resulting images may be recorded by a video camera, so that the temporal resolution is 20 ms while the spatial resolution is of the order of 100 nm.

From the rich variety of spatial patterns observed so far, in the following only a few typical examples will be shown. It should be mentioned that all these data were recorded in situ during operation of the catalytic reaction at fixed control parameters ($p_{O_2}$, $p_{CO}$, $T$). The images correspond to sections of the sample surface with 0.4 mm diameter; dark areas reflect oxygen covered regions, while those predominantly covered by adsorbed CO appear grey.

At lower temperatures (~ 480 K) spatial self-organisation is governed by surface diffusion/reaction and hence the associated spatio-temporal patterns exhibit properties of propagating waves. In fig. 9a these waves are of the type of growing spirals which typically originate at defect sites on the surface. Under somewhat different conditions, concentric wavefronts are emanated in periodic intervals from certain pacemakers (fig. 9b). These patterns are closely reminiscent to those observed with the quoted Belousov-Zhabotinskii reaction operated in a flat Petri disk without stirring the solution. In both examples of fig. 9 the patterns are not circular, but elliptically shaped. The long axis of these ellipses is along the [110]-direction of the Pt(110)-surface (see fig. 3), and this effect reflects the anisotropy of the surface diffusion coefficients of adsorbed species on this plane.

The data of fig. 6 had been recorded at higher temperature, at which rapid regular oscillations and their transition to chaotic behavior is observable. Under these conditions spatial self-organisation is no longer governed by diffusion/reaction, but rapid (~ $10^{-4}$ s) synchronisation occurs through the gas phase, so

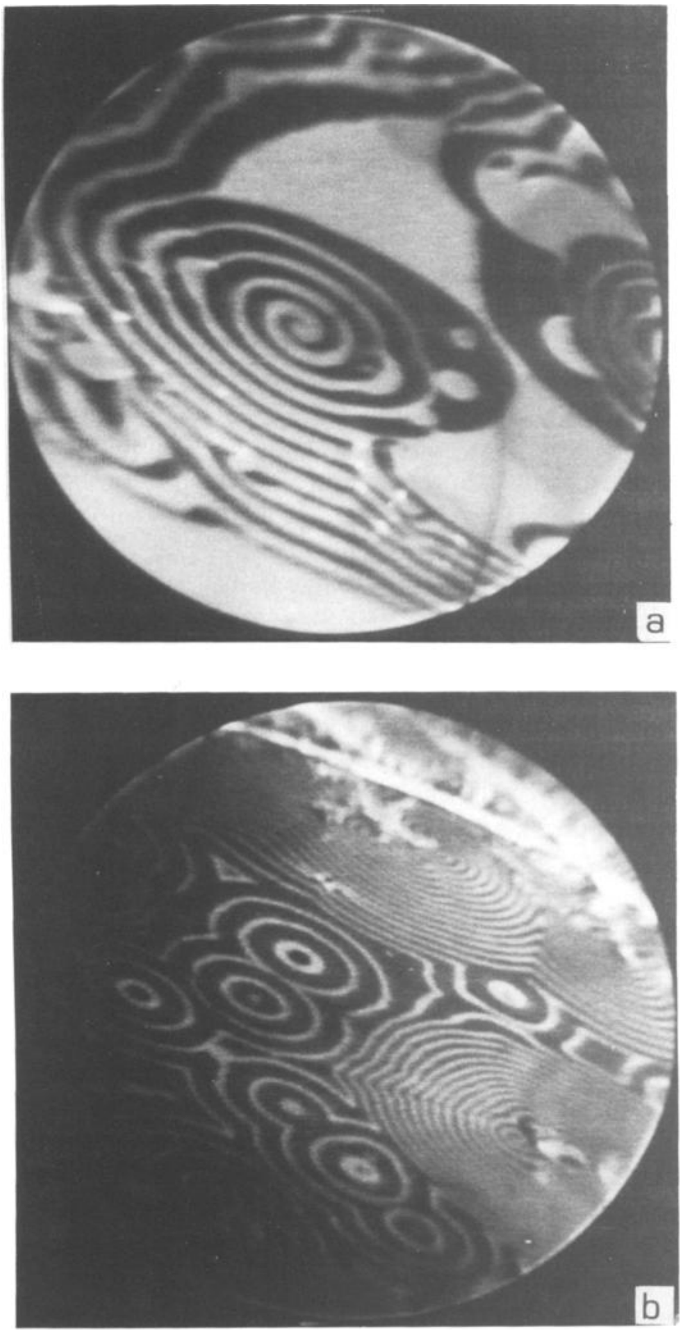


Fig. 9. Spatio-temporal patterns on Pt(110) as imaged by PEEM. a) $T = 435$ K, $p_{O_2} = 3.0 \times 10^{-4}$ mbar, $p_{CO} = 2.8 \times 10^{-5}$ mbar; b) $T = 430$ K, $p_{O_2} = 3.2 \times 10^{-4}$ mbar, $p_{CO} = 3.0 \times 10^{-5}$ mbar.

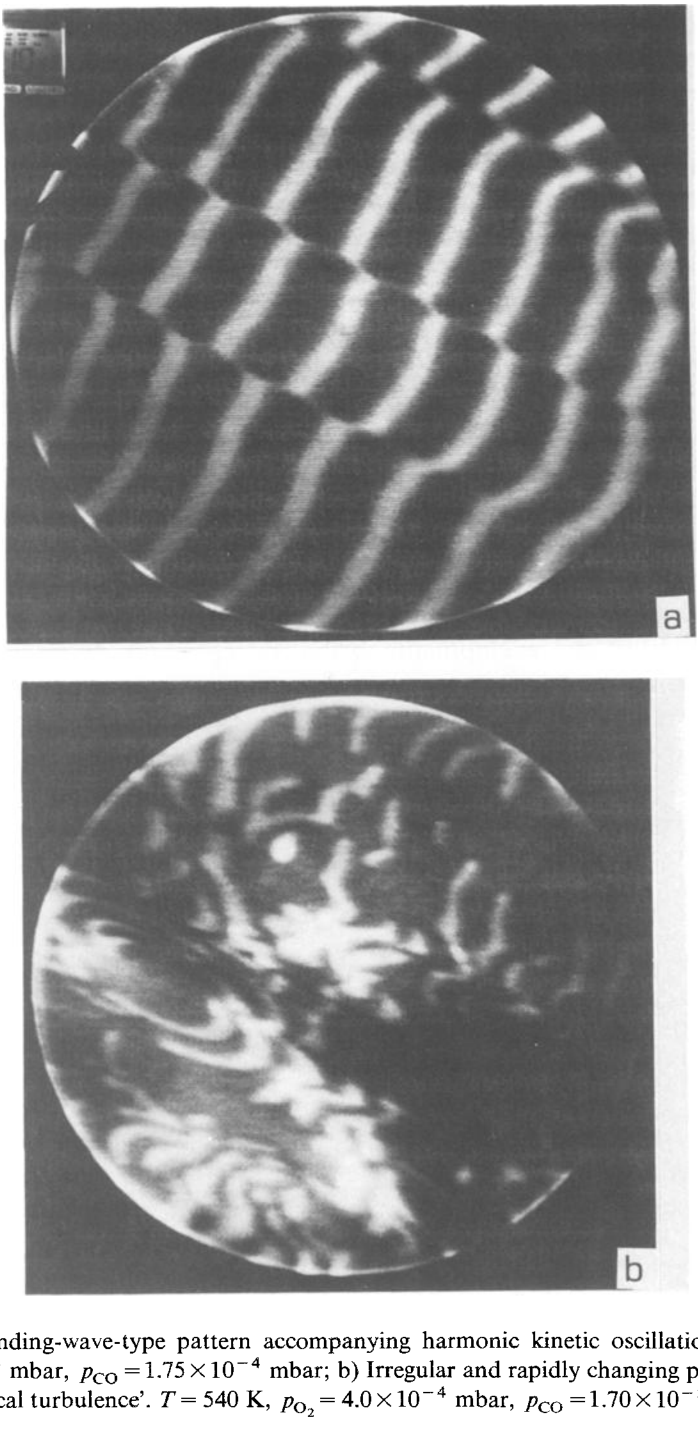


Fig. 10. a) Standing-wave-type pattern accompanying harmonic kinetic oscillations. $T = 550$ K, $p_{O_2} = 4.1 \times 10^{-4}$ mbar, $p_{CO} = 1.75 \times 10^{-4}$ mbar; b) Irregular and rapidly changing pattern reflecting 'chemical turbulence'. $T = 540$ K, $p_{O_2} = 4.0 \times 10^{-4}$ mbar, $p_{CO} = 1.70 \times 10^{-5}$ mbar.

that different parts of the surface oscillate in phase. The patterns associated with harmonic temporal oscillations are standing waves of the type for which a 20 ms snapshot is reproduced in fig. 10a. The whole surface exhibits approximately equally spaced alternating dark ($O_{ad}$) and bright ($CO_{ad}$) stripes whose relative intensities vary rapidly with the period of the associated kinetic oscillation ( ~ 2 sec). Slight deviations from the constant spacing between these stripes lead to the formation of dynamic 'dislocations' as evident in fig. 10a.

The transition to temporal chaos upon stepwise variation of one of the control parameters (cf. fig. 6) is associated with a transition to more irregularly shaped stripe patterns, until the stripes break up and perform rapid movements (fig. 10b). These spatio-temporal patterns closely resemble a turbulent fluid so that the term 'chemical turbulence' may be used to characterize this state of spatial chaos. It has to be emphasized, however, that turbulence of a fluid comprises hydrodynamic convection while in the present case it is just a consequence of the interplay of adsorption, desorption and reactive interaction of two species in a strictly two-dimensional surface phase.

Phenomena of the illustrated type might be existent with many (if not all?) catalytic reactions. Frequently their existence will be restricted to rather narrow ranges of reaction conditions, and their manifestation will mostly be further masked by inhomogeneities of the surface structure as well as of the control parameters. Nevertheless it is felt that these effects will have to be taken into consideration for further developments of the concepts underlying the kinetics of catalytic reactions.

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