

Cellular Structures in Catalytic Reactions with Global Coupling

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By employing mirror electron microscopy (MEM) to image the Pt(110) surface during the catalytic oxidation of CO we observe that a fine cellular structure (typical dimension 1–5 μm) develops under conditions at which rate oscillations occur. Based on an analysis using the complex Ginzburg-Landau equation, it is demonstrated that such a structure forms generally in an oscillatory medium in the presence of global coupling. [S0031-9007(96)00111-1]

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Global coupling plays an important role in a large number of dynamical systems ranging from the biological [1,2] and chemical [3] to phenomena more familiar to physicists such as gas discharges and transport processes in semiconductors [4–6]. Its effect can also be studied in oscillatory catalytic surface reactions where different reacting parts of a surface are coupled via partial pressure variations in the gas phase. In these reactions a large variety of spatiotemporal patterns have been observed in low pressure ($p < 10^{-3}$ mbar) single crystal experiments [7,8] using photoelectron emission microscopy (PEEM), a technique which allows parallel imaging of the surface with, typically, a field of view of 200 μm and a resolution of 1–10 μm [9]. Global coupling results in a type of pattern that is not seen in simple reaction-diffusion systems and has the form of a standing wave. An example is provided by the oxidation of CO on a Pt(110) surface [10–13]. Using mirror electron microscopy (MEM) at a resolution better than 0.1 μm we report in this Letter the observation of a fine cellular structure which develops during the latter reaction. We attribute the formation of such a structure to global coupling since it only exists under conditions at which rate oscillations are observed. Using simulations based on the modified complex Ginzburg-Landau (CGL) equation, which describes an oscillatory medium, we demonstrate that a cellular structure similar to the one seen in the experiment can indeed be observed if global coupling is taken into account.

During catalytic CO oxidation molecular oxygen readily dissociates on the Pt(110) surface into adsorbed atomic oxygen (O_{ad}) which reacts with adsorbed CO (CO_{ad}) to form the product CO_2 which in turn rapidly desorbs from the surface. Rate oscillations arise in this system through the coupling of the reaction with the $1 \times 1 \leftrightarrow 1 \times 2$ phase transition which is controlled by a critical coverage of CO [8].

As in previous investigations we study the reaction under isothermal conditions at low pressure ($p < 10^{-3}$ mbar) such that the UHV system is operated as a gradient-free flow reaction. Global coupling is present under these conditions as a consequence of mass

balance in the reaction system requiring that oscillations in the reaction rate are accompanied by variations in the partial pressures of the reactants (typically ca. 1% of p_{CO}) [7,8,14]. The MEM measurements were performed in a low energy electron reflection microscope essentially similar to the instrument described by Teliëps and Bauer [15]. MEM is extremely sensitive to both surface topography and differences in work function; it provides sufficient intensity for high temporal (0.04 s) and spatial ($\leq 0.1 \mu\text{m}$) resolution. The method is thus ideally suited for investigations of dynamic phenomena at surfaces [16,17]. The electron energy in the present experiments was chosen such that depending on the local work function some electrons actually penetrate the surface and are not reflected. Areas with low work function then appear black, i.e., the contrast relative to PEEM is reversed. The Pt(110) sample used was freshly prepared and cleaned by a combination of Ar ion sputtering, heating in oxygen at 700 K ($p_{\text{O}_2} = 1 \times 10^{-5}$ mbar) and annealing to 950 K.

For partial pressures of the reactants in the 10^{-5} mbar range at $T = 430$ K, the reaction rate was initially stationary and target patterns as well as rotating spiral waves were observed [10,17]. For a certain set of parameters, however, the rate did not remain stationary but oscillations developed within a few minutes. These were accompanied by the formation of the spatiotemporal patterns shown in Fig. 1. The first frame shows an oxygen-covered Pt(110) surface with a large structural defect imaged as a dark circular area. The step bunch structure of the surface is clearly visible [16,18]. Small CO islands, which are imaged as dark areas, now begin to nucleate (frame 2) and, as they grow, a cellular structure develops (frame 3). This is more clearly seen in frame 4. (Note that in PEEM the reverse contrast pertains: oxygen-covered areas are dark and CO-covered areas light [10].) A network of thin bright lines (“membranes”), which do not necessarily coincide with the step bunch structure, divides the CO-covered surface into an array of individual cells. The cells then merge (frame 5) and a relatively uniform state of the CO-covered surface is established. After that the surface gradually returns to the state where it is covered with oxygen (an

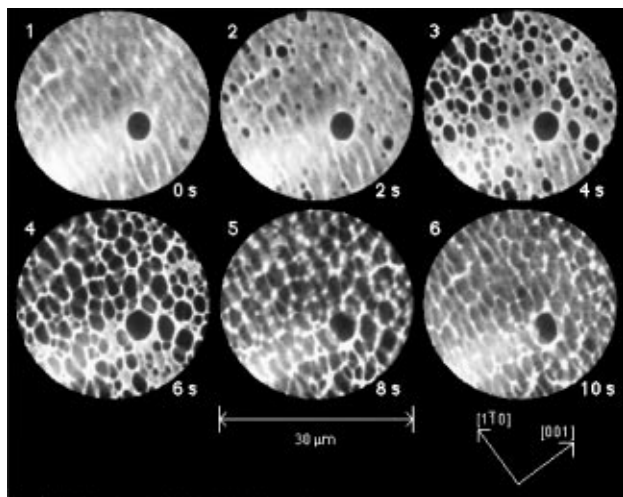


FIG. 1. MEM images showing the development of a cellular structure during rate oscillations in catalytic CO oxidation on Pt(110). Depicted is a cycle of 10 s duration which is smaller than the period of the rate oscillations (24 s). Experimental conditions: $T = 430$ K, $p_{\text{CO}} = 0.54 \times 10^{-5}$ mbar, $p_{\text{O}_2} = 1.3 \times 10^{-5}$ mbar.

intermediate stage is shown in frame 6). In this particular experiment the cycle just described took 12 s and, subsequently, the surface remained oxygen covered for another 11 s. Then, in a very rapid cycle of only about 1 s duration, the surface again goes through the sequence of patterns displayed in Fig. 1 but in the reverse order. The total time of 24 s is also the period observed for the measured rate oscillations corresponding to some kind of integral behavior over the whole surface.

The process through which global coupling gains control over the reacting surface is illustrated in Fig. 2. The first frame shows the situation where the reaction rate is still stationary and target patterns are present on the surface. With the onset of oscillatory behavior, the target pattern breaks up and a complex pattern of propagating waves is formed (frame 2). Subsequently, small CO islands begin to nucleate in the region directly in front of the propagating CO wave (frame 3). This further results in the complete disintegration of the CO waves and leads to the formation of the cellular structure shown above in Fig. 1. The whole process can be regarded as an induction period since the development of the rate oscillations takes place without any further change of the parameters.

For understanding the nature of the cellular structure, it is important to note that the network only forms when rate oscillations develop, i.e., when global coupling is effective. In this respect, the situation resembles the occurrence of standing waves that were found earlier in the same system at higher temperature (540–550 K) [10]. However, in contrast to the standing waves which form a rapidly oscillating stripe pattern with a wavelength of ca. 20–50 μm and a period of a few seconds, the cellular

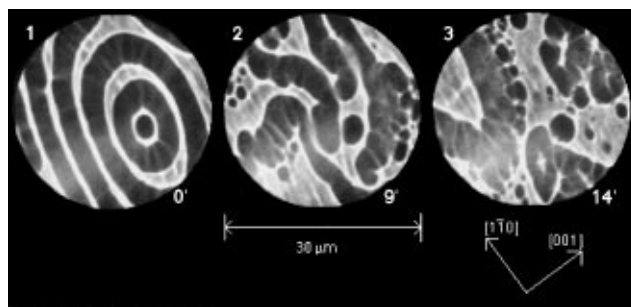


FIG. 2. Transformation of a target pattern into a cellular structure occurring as rate oscillations develop, time in minutes. Experimental conditions essentially identical with those of Fig. 1.

structure exhibits a characteristic size of about 1 μm and a period of the order of 1 min.

In the experiment shown in Fig. 1 the cellular structure was observed to stay at exactly the same position for over 80 oscillatory cycles (ca. 30 min), showing that the structure is probably pinned by the structural defects of the substrate. On the other hand, the propagation of the chemical waves is not significantly influenced by structural defects, as shown by the smooth boundaries of the fronts in frame 1 of Fig. 2. Further, the structure of the “membranes” does not necessarily correspond to that of the surface microtopography, as we have noted above. We thus conclude that although the cellular structure may be pinned by the defects, their influence alone is not a sufficient explanation of the origin and properties of the structure and that the effects of global coupling have to be taken into consideration.

In order to demonstrate that global coupling can indeed lead to cellular structures we have performed simulations with the CGL equation which we have modified to take global coupling into account. Our previous investigations of this model have shown that it describes qualitatively the various effects of global coupling in oscillatory systems, such as the breakdown of synchronization caused by defects [19,20], spontaneous formation of phase domains [20], and development of standing waves [13].

The modified CGL equation is given by

$$\dot{\eta} = (1 - i\omega)\eta - (1 + i\beta)|\eta|^2\eta + (1 + i\varepsilon)\nabla^2\eta + \mu e^{i\chi}\bar{\eta}, \quad (1)$$

where

$$\bar{\eta} = \frac{1}{S} \int \eta(\mathbf{x}, t) d\mathbf{x} \quad (2)$$

is the spatial (surface) average of the local complex oscillation amplitude $\eta(\mathbf{x}, t)$ and S is the total surface area. This equation describes a population of small-amplitude limit-cycle oscillators which are coupled both locally (due to diffusion) and globally. The nonlinearity in a single oscillator is specified by the parameter β ,

while the local coupling is characterized by the parameter ε . The last integral term in Eq. (1) can be interpreted as a driving force that is produced collectively by all oscillators in the population and applied back on each of them. The intensity of global coupling is characterized by the coefficient μ ; the factor χ in the last term takes into account a phase shift between the driving force and the average amplitude $\bar{\eta}$.

If the condition $1 + \varepsilon\beta < 0$ is satisfied, uniform oscillations in this system are stable at sufficiently strong intensities μ of global coupling inside a window of the parameter χ . When μ is decreased, they first become unstable with respect to the growth of a mode with a certain wave number k_0 and the same frequency as that of uniform oscillations [12]. The growth of this mode is limited due to further nonlinear interactions. In a two-dimensional system, a simple extension of such a mode yields a periodic stripe pattern. Although such patterns are occasionally seen in our numerical simulations, the typical pattern is a hexagonal array of cells, as in the case of external periodic forcing [21]. The origin of a cellular structure lies in the fact that, in two dimensions, the whole family of modes with the wave numbers \mathbf{k} satisfying the condition $|\mathbf{k}| = k_0$ becomes simultaneously unstable. The nonlinear interactions may then enhance the growth of triplets of such modes with wave vectors satisfying the condition $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$. These give rise to a hexagonal cellular structure (Fig. 3).

In contrast to cellular structures formed by a Turing instability in chemical reaction-diffusion systems [22,23], a cellular structure in the oscillatory system considered does not correspond to a stationary distribution of reactants. In such a pattern, both the modulus of the local oscillation amplitude and its phase are spatially modulated.

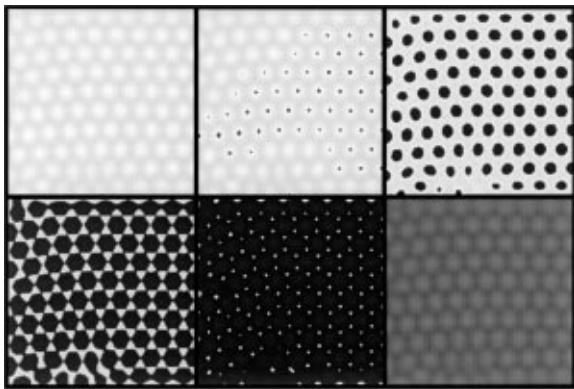


FIG. 3. Time-dependent cellular structure obtained by numerical integration of Eq. (1) with $\beta = -1.4$, $\varepsilon = 2.0$, $\mu = 0.245$, $\chi = 1.8\pi$, and $\omega = 0.1$ for the system of linear size $L = 100$ with no-flux boundary conditions. Spatial distributions of the local oscillation phase $\phi(x, t) = \arg[\eta(x, t)]$ at subsequent time moments within one oscillation cycle are shown (from top left to right bottom). The phase varies from 0 to 2π and the darker regions correspond to its smaller values.

We have found that oscillations in different cells are synchronized in time. Starting from random initial conditions, irregular patterns representing strongly distorted hexagonal arrays are produced (the relatively regular pattern shown in Fig. 3 is obtained after a long transient process). The characteristic time scale for motion of cell boundaries in the process of relaxation towards a more ordered state are, however, much larger than the oscillation period.

Comparing the typical evolution of a cellular structure in Fig. 3 with the behavior of cellular structures in the experiment, a number of similarities can be noted. As a new cycle of oscillations begins, small “islands” are formed in the centers of the cells (frame 2 in Fig. 3). They grow (frame 3) and form a hexagonal network (frame 4). After that, the islands merge (frame 5) and a relatively uniform state (frame 6) is established. This state then gradually transforms into the initial state shown in the first frame. However, there is also a difference. Each cycle in the experiment consists of two subcycles of significantly different durations. The model (1) is constructed assuming oscillations are almost harmonic; it therefore cannot reproduce such more complex situations. Only the main part of the experimental cycle thus agrees with the simulation.

The exact nature of the cellular pattern in terms of surface structure and adsorbate coverages in the system Pt(110)/CO + O₂ is not yet quite clear. Although the pressure range of our experiment was below ca. 10^{-4} mbar beyond which a faceting of the Pt(110) surface is known to occur, it cannot be ruled out that a certain amount of reaction-induced roughening (on a microscopic length scale) might play a role [24,25]. This would not, however, invalidate our theoretical analysis as long as the structure still originates from the effect of global coupling on an oscillatory medium and not from specific properties of the system investigated.

In summary, by employing MEM we have demonstrated that a cellular structure develops under oscillatory conditions in the system Pt(110)/CO + O₂. Since a theoretical analysis with a rather general model yields similar cellular structure, we conclude that the experimentally observed structure represents a new type of pattern existing in oscillatory media in the presence of global coupling. Analogous patterns can be expected in other systems.

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