Solitons in a Surface Reaction

H. H. Rotermund, S. Jakubith, A. von Oertzen, and G. Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, W-1000 Berlin 33, Germany
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The catalytic oxidation of CO on Pt(110) exhibits, for certain sets of control parameters, oscillatory kinetics and spatiotemporal pattern formation which may be followed by photoemission electron microscopy. Within a very narrow range of conditions, these patterns consist of solitary waves with bell-shaped profiles which propagate with a constant velocity of about 3 μm/s along the crystallographic [001] axis of the surface. Collision of pulses traveling in opposite directions leads mostly to annihilation, but in some cases the two waves emerge again with unchanged shapes and velocities, as characteristic for solitons.

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A solitary wave denotes a plane-wave pulse which translates in one direction without changing its profile. If such a solitary wave preserves its shape and speed after collision with another one, it is defined as a soliton.[1,2] Solitary waves have been observed in various fields, ranging from hydrodynamics[3] to arrays of coupled electrical oscillators[4] or to atmospheric perturbations.[5] Theoretically these effects are usually described by nonlinear evolution equations (such as the Korteweg–de Vries or sine-Gordon equations). The appearance of time-independent wave profiles may be attributed to a balance between nonlinearity and dispersion.

A quite different class of nonlinear, *dissipative* phenomena is found with certain types of chemical reactions which are described in terms of reaction-diffusion (RD) equations.[6] Although a set of RD equations could be constructed in a way that its solutions may contain solitons,[7] experimental verification with a chemical system has, to our knowledge, so far not yet been demonstrated. We report here on observations with a surface reaction, the catalytic oxidation of carbon monoxide on a Pt(110) single-crystal surface, which is associated with the formation of spatiotemporal patterns.[8] In the course of these studies solitary-wave-type patterns were also found to develop under special conditions, among which a small fraction exhibits all the properties characterizing solitons, while the majority of collisions, on the other hand, leads to annihilation of one of the pulses.

The catalytic oxidation of CO on platinum proceeds through recombination of chemisorbed carbon monoxide and (atomic) oxygen. These surface species are supplied by adsorption from the gas phase, and as a consequence their surface concentrations (i.e., coverages) Θ_{CO} and Θ_O are determined by the respective partial pressures, p_{CO} and p_{O_2}, and by the temperature T. On the Pt(110) surface, under steady-state flow conditions and for certain ranges of these control parameters the rate of CO_2 formation is not stationary, but may become oscillatory or even chaotic. These kinetic phenomena have been explored in detail[9] and have been successfully modeled in terms of a system of coupled nonlinear ordinary differential equations describing the elementary steps involved.[10]

In a reaction-diffusion system, however, only within small local elements may the state variables be viewed as being solely dependent on time, while a macroscopic system (i.e., the single-crystal surface with about 0.5-cm^2 area) has to be considered as an assembly of such local diffusion-coupled regions. As a consequence, the coverages Θ_i become dependent on time *and* location, leading to the above-mentioned spatiotemporal pattern formation.

Spatial differences of the coverages Θ_{CO} and Θ_O were imaged by means of a recently developed photoemission electron microscope (PEEM),[11] whose image contrast is based on the different dipole moments of the adsorbate complexes O_{ad} and CO_{ad}, giving rise to respective differences of the local work function. In particular, in the images reproduced below, O-covered areas appear dark, while those covered by CO are grey. The PEEM instrument in its present version has a lateral resolution of about 0.1 μm. Images are taken from a fluorescence screen by means of a charge-coupled-device camera and stored on video tape, with 20 ms required for recording a single image. The experiments were performed within an UHV system under steady-state flow conditions of the reactants with partial pressures in the 10^{-4}-mbar range. Further details are described elsewhere.[8,11] All the data presented here were recorded for a particular set of external conditions, $p_{O_2}=3.5\times10^{-4}$ mbar, $p_{CO}=1.0\times10^{-4}$ mbar, $T=485$ K, and the phenomena to be described were confined within a very narrow range of control parameters.

Waves formed by elongated dark regions due to enhanced oxygen coverages were found to propagate across the surface. Figure 1 displays two PEEM images recorded with a time interval of 3.0 s from a 130×70-μm^2 area of the surface. The width of the "pulses" is about 2.5 μm, while their length is typically in the 30-μm range. Pulses with smaller length were found to be unstable and to dissolve gradually, while longer ones, on the other hand, apparently did not form. We observed that

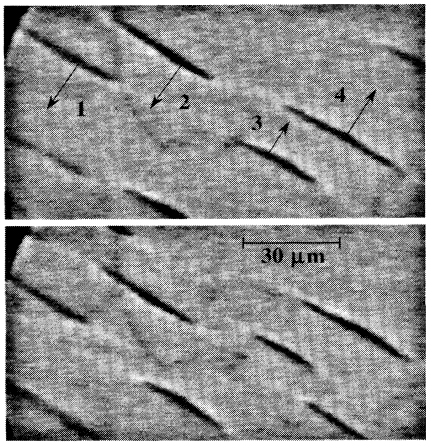

FIG. 1. PEEM images, taken with an interval of 3 s, from a Pt(110) surface under steady-state conditions of catalytic CO oxidation. The dark objects are regions with enhanced O_{ad} coverage which move along the indicated directions with constant velocity.

these pulses always propagate in the same direction (either forward or backward) coinciding with the crystallographic [001] direction of the Pt(110) substrate, and are elongated in the perpendicular [110] direction. The Pt(110) surface exhibits twofold symmetry with pronounced anisotropy of the surface diffusion of adsorbed species along the two main crystallographic axes indicated, and it is presumably this anisotropy which constrains the motion essentially to a one-dimensional problem under the present conditions.

Figure 2 shows, for selected pulses, a plot of the position along the axis of motion as a function of time. The resulting straight lines indicate constant velocities of propagation of each of the waves, and the fact that these lines are parallel to each other reflects the fact that all waves move with the same velocity, evaluated as $v = 3.2 \pm 0.2$ μm/s. Figure 3 shows a typical wave

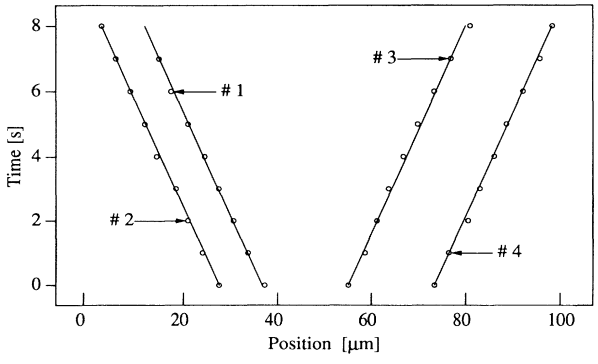

FIG. 2. Variation with time of the position of the solitary waves marked in Fig. 1 along their respective axis of propagation. The slopes yield a velocity of $v = \pm 3.2$ μm/s.

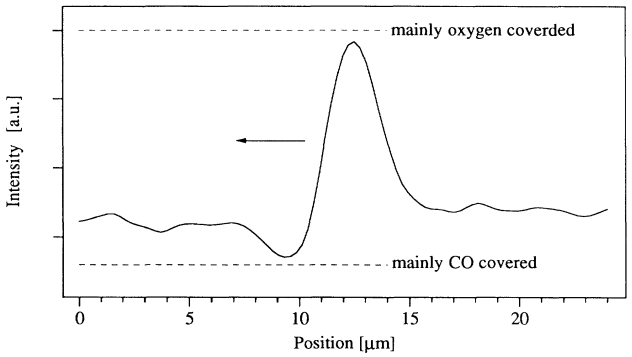

FIG. 3. (Negative) intensity profile of a solitary wave along its direction of propagation.

profile, namely, the degree of darkening (equal to negative intensity of electron emission in the PEEM image) in a section along the direction of propagation. It should be noted that propagation occurs always in that direction which exhibits a dip in negative intensity, as reflected by the bright zones in front of the pulses. The intensity profile is nearly bell shaped and remains essentially unchanged with time, as characteristic for a solitary wave.[2] In contrast, chemical waves, e.g., as reported for the Belousov-Zhabotinsky reaction, are usually found to have profiles that are rather asymmetric, with sharp fronts and extended tails.[12]

In most cases of head-on collisions of pulses traveling in opposite directions, one of the pulses is extinguished and the other one propagates with the same velocity as before. Sometimes mutual annihilation occurs, and in rare cases events characteristic of soliton behavior are observed. Figure 4 displays a series of sections from PEEM images of a 10×30-μm^2 area taken at intervals of 1.1 s: Two waves approaching each other merge upon collision, and after some time separate and move apart again.

The sequence of associated wave profiles is reproduced in Fig. 5. Here it becomes evident that during collision the combined system retains high intensity (but less than the *sum* of the two separate waves), from which again two waves emerge moving apart from each other. A plot

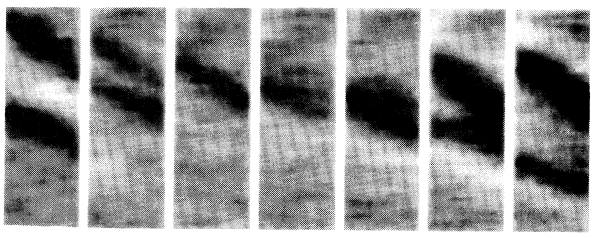

FIG. 4. A sequence of PEEM images recorded at intervals of 1.1 s from the same section of the surface, illustrating the collision of two pulses followed by their reappearance, as characteristic of a soliton.

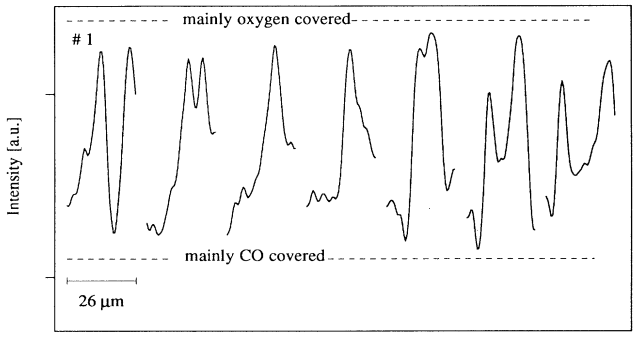

FIG. 5. Intensity profiles along the propagation direction from the PEEM images displayed in Fig. 4.

of the position of the intensity maxima as a function of time (similar to the data of Fig. 2) is shown in Fig. 6. It demonstrates that the two waves travel with the same velocities before and after the collision. The central part of the figure represents the region of the collision in space and time.

This observation exhibits all the properties of a soliton as defined in the original paper of Zabusky and Kruskal[1] on the basis of numerical solution of the Korteweg–de Vries equation: The pulses are bell shaped and translate with constant velocity. "They can exist in close proximity and interact without losing their form or identity (except momentarily while they overlap substantially). In other words, solitons 'pass through' one another."[1]

Nonlinear chemical reactions (like the present system) are generally modeled in terms of reaction-diffusion equations of the type

$$u_t = Du_{xx} + F(u) ,$$

where u is the vector of concentration variables and D is a diagonal matrix of transport (diffusion) coefficients. Systems described by such equations are often interpreted in terms of an excitable medium: This means a dynamic system which can pass from a receptive into an excited state by a perturbation, from which it transforms into a refractory state (in which no renewed excitation is possible) and after some time it returns into the receptive state. Experimental verification of the formation of such trigger waves by external perturbation (by means of a laser pulse) was, for example, recently performed with the present reaction occurring on another platinum single-crystal surface, (100).[13] So far, however, no solitary waves had been observed with chemical systems, and it had been the common belief[14] that a collision between two fronts of excitation would lead to their mutual annihilation, as was indeed only observed in a few of the encounters of the present study.

Stationary (i.e., fixed in time) solitary patterns have been experimentally observed with gas-discharge systems and with electrical networks, for which a satisfactory theoretical description could, on the other hand, be obtained by suitable RD equations based on the concept of excitable media.[15] True solitons were found in the solutions of an admittedly artificial two-variable system of RD equations.[7] Another noteworthy result of this latter work was that in a collision between slightly asymmetric solitary waves, only one survived, and generally there existed a pronounced tendency for mutual extinction, just as was observed experimentally in the present study. It is believed that modeling of the present system by a set of RD equations based on knowledge about the underlying reaction steps will also lead to solitary waves and soliton solutions under special conditions. Work in this direction is currently in progress.

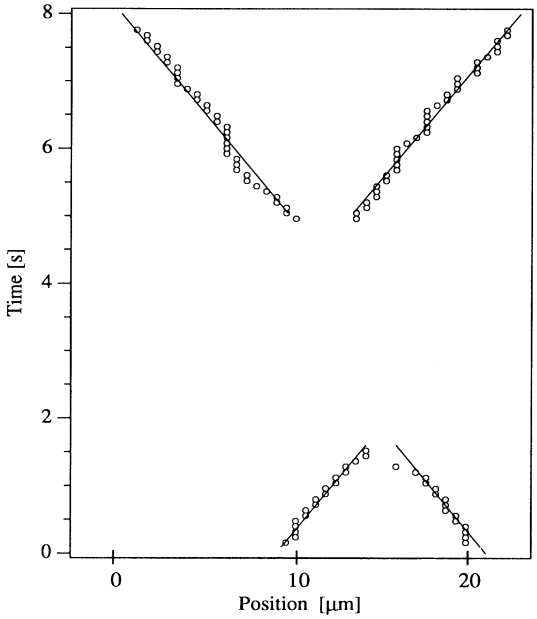

FIG. 6. Position of the intensity maxima of the two pulses of Fig. 4 as a function of time. The central region marks the collision zone which continues to propagate; hence there is no direct continuation of the straight lines in the lower and upper parts.

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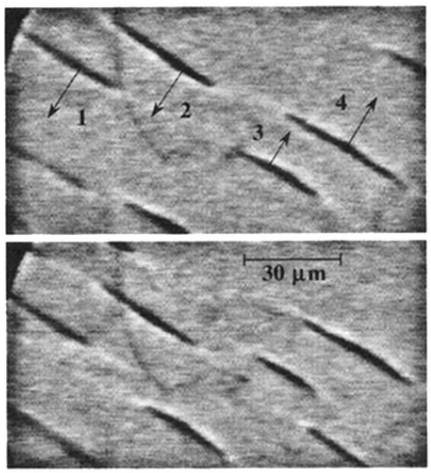

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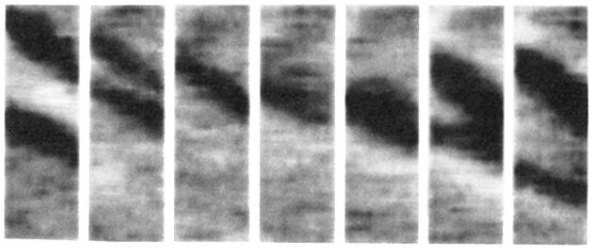

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