A New Type of Traveling Interface Modulations in a Catalytic Surface Reaction

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A new type of traveling interface modulations has been observed in the NH$_3$ + O$_2$ reaction on a Rh(110) surface. A model is set up which reproduces the effect, which is attributed to diffusional mixing of two spatially separated adsorbates causing an excitability which is strictly localized to the vicinity of the interface of the adsorbate domains.

Pattern formation in reaction-diffusion systems covers a wide range of fascinating phenomena in liquid phase chemistry, biochemistry, biology and catalytic surfaces [1–3]. In general, the patterns arise due to the coupling of a non-linear reaction term with diffusion. Reaction fronts, target patterns and spiral waves, stationary concentration patterns and chemical turbulence have been seen. Various additional factors like global coupling, diffusional anisotropy, energetic interactions and cross diffusion of reactants may add to the complexity and diversity of the chemical wave patterns.

Extended bistable systems generically exhibit fronts (also called interfaces or domain walls) connecting one phase in one part of the spatial domain to the other phase in some other part of the domain. In two spatial dimensions the most natural geometry is a straight line for the front position, suitably defined as some intermediate level curve of the solution. However, already in simple bistable systems, initially straight interfaces between two domains may undergo a number of instabilities, see, e.g., [4, Chapter 2] for an overview. A typical case is a linear transverse instability leading to a regular (periodic) or irregular bending of the front, but with small amplitude, which may then often be described by Kuramoto-Sivashinsky type of equations, see [5]. Another possibility is that an instability does not saturate at some small amplitude, which may yield “fingering” and labyrinthine patterns [6–8]. Similar wave instabilities also occur in excitable media, see, e.g., [9].

Here we report on a new type of instability and self-organization of an interface, namely interface modulations that originate from corners and travel along the interface in a pulse like fashion, leaving the interface position almost unperturbed behind. These excitations have been observed in the NH$_3$ + O$_2$ reaction on a Rh(110) surface. The effect is attributed to diffusional mixing of two spatially separated adsorbates causing an excitability which is strictly localized to the vicinity of the interface of the adsorbate domains. Combining a bistable with an excitable system, we set up a general model which reproduces the traveling interface modulations seen in the experiment.

The reaction we study is the catalytic ammonia oxidation with O$_2$ on a Rh(110) surface under low pressure conditions ($10^{-5}$ mbar) in a UHV chamber equipped with a photoemission electron microscope (PEEM) as spatially resolving method. Illuminated with a D$_2$ discharge lamp (5.5–6 eV) photoelectrons are ejected which allow an imaging of the local work function with a spatial resolution of $\approx 1\mu$m and the temporal resolution of video images (20 ms). At elevated temperatures (T > 400 K) both reactants dissociate upon adsorption into their atomic constituents O$_{ad}$, N$_{ad}$, and H$_{ad}$ [10, 11]. The atomic adsorbates recombine, forming N$_2$, NO, and H$_2$O as main products. Also, H$_2$ is produced and desorbs at a high rate, and hence the coverage $\theta_H$ is always small. The adsorbates N and O form a large number of ordered reconstruction phases on Rh(110) but under our reaction conditions only the (2×1)-N/(3×1)-N corresponding to $\theta_N = 0.5/0.33$ and the c(2×6)-O corresponding to $\theta_O = 0.66$ are relevant [12]. In addition, a mixed coadsorbate phase c(2×4)-2O,N may form.

Over a broad range of parameters the reaction exhibits simple bistability, i.e. one observes a broad hysteresis in the reaction rates in heating/cooling cycles. The reactive branch is associated with the (2×1)/(3×1) of nitrogen, the unreactive branch with the c(2×6) of oxygen. Transitions between the two states occur via fronts. If one adjusts conditions close to equistability both phases are simultaneously present as shown by the PEEM image in Fig.1a. Since oxygen adsorption strongly increases the
work function (WF) ($\Delta \Phi_{\text{max}} \sim 1.0 \text{eV}$) high O$_{ad}$ coverages are imaged dark whereas adsorbed nitrogen which only causes a maximum WF increase of 280 meV appears bright [13].

The position of the interface is nearly stationary but one notices small lateral displacements of the interface which emanate near the sharp corner in the phase boundary and then propagate in a pulse-like manner along the interface. This process is depicted in more detail by the frames in Fig.1b displaying an enlarged section of the PEEM image in (a). The velocity of the pulse-like excitations is about 6 µm/s. Cross sections of the interface showing the temporal variation of the interface positions at two different points, E and S, are displayed in Fig.1c. Near the sharp corner, in point S, the amplitude is below the detection limit. Further away, at point E, the amplitude is substantial varying between a few µm and 20 µm. One notes a drift of the average interface position of about 15 µm over an observation time of 170 s which is due the fact that the equistability conditions are not exactly met. The time series exhibits irregular behavior but the excitability of the interface is quite stable and can be observed over several hours. The average period of the local excitations is around 10 s. In our experiments we found no correlation between the interface angles and interface excitations, and the crystallographic directions of the surface.

In order to understand why the excitations remain localized at the interface and do not extend into the interior of the phase it is helpful to look into the chemically rather similar system Rh(110)/NO + H$_2$ which can be considered as well understood [13, 14]. Some spectacular chemical wave patterns including rectangularly shaped target patterns and spiral waves and traveling wave fragments were found there. The excitable behavior in this system was shown to be based on a cyclic change of three different structures; the c(2×6)–O of oxygen, the (2×1)/(3×1)–N of nitrogen and the c(2×4)–2O,N as mixed coadsorbate phase. In the NH$_3$ + O$_2$ reaction only two of these three structures are present as stable phases while the mixed coadsorbate phase is missing. Apparently the mixed phase does not form by coadsorption.

If we assume that by surface diffusion this mixed phase may form, its formation is restricted to a boundary layer along the interface where the two separated adsorbates, N and O, can penetrate each other by diffusion. Excitability would then be strictly restricted to a boundary region along the interface and this is what we basically see in the experiment. Using the diffusion values which have been used for quantitative simulation of the chemical wave patterns in Rh(110)/NO + H$_2$ we can estimate the diffusion length $l$ at T=740 K for $\tau=10$ s with $l = \sqrt{2D\tau}$ resulting in $l = 8 \mu$m for N and $13 \mu$m for O [13].

The inset in Fig. 1a shows a dark boundary region of a few $\mu$m width which is consistent with the high WF of 1.1 eV of the c(2×4)–2O,N phase [15].

For modeling the observed behavior we set up a dimensionless 3-variable model for bistable/excitable media which in 2D reads

$$\partial_t u = u - u^3 - v - \delta(u-u_s)q^2 + d_u \Delta u + d_{aq} \Delta q,$$  

$$\partial_t v = \varepsilon(u + \beta - v) + d_v \Delta v,$$  

$$\partial_t q = (1 - q)(q - a)(q + 1) + \gamma(1 - q^2)(u - u_s) + d_{aq} \Delta u + \Delta q,$$

with diffusion constants, $d_u, d_{aq}, d_v > 0$, parameters $\beta, \gamma, \delta \in \mathbb{R}$, $\varepsilon > 0$ and $-1 < a < 1$. In short, using $U = (u, v, q)$ with obvious notations we write

$$\partial_t U = f(U) + D \Delta U.$$  

The system (1) is composed of an excitable $u, v$–subsystem (FHN like) and a bistable $q$–subsystem (Allen–Kahn or Nagumo equation), which has front solutions.

The basic idea is that (i) through the interaction with the $q$-variable the $u, v$-subsystem is excitable only in the
vicinity of the front position (where $q \approx 0$), and that (ii) these localized excitations of the $u,v$-subsystem then push or pull the $q$-front. Since on surfaces the diffusion of the different species is not independent of each other, we include cross-diffusional terms which have to be symmetric according to Onsager's reciprocity relation. On surfaces cross diffusion arises (i) due to the vacant site requirement for diffusional hops and (ii) due to energetic interactions between coadsorbed species [16, 17]. In particular, the strong repulsive interaction between coadsorbed oxygen and nitrogen shows up in a downward shift in the $N_2$ desorption maximum by about 100 K [18]. As will be shown below cross-diffusion becomes important for the nucleation of excitation pulses.

Thus, we choose parameters $\beta, \varepsilon$ in such a way that in the absence of $q$, i.e., for $q \equiv 0$, the $(u,v)$ ODE subsystem $\partial_t(u,v) = (f_1(u,v,0), f_2(u,v,0))$ is excitable. Its unique ODE fixed-point $(u_\ast, v_\ast)$ is given by $u_\ast = -\beta^{1/3}$, $v_\ast = u_\ast + \beta$. This fixed point is asymptotically stable and globally attracting, but for small $\varepsilon > 0$ rather small perturbations may lead to large excursions.

For $u \equiv u_\ast$, or equivalently $\gamma = d_{uu} = 0$, (1c) is a standard bistable equation

$$\partial_t q = g(q) + \Delta q, \quad g(q) = (1 - q)(q - a)(q + 1),$$

i.e., the kinetics $\partial_t q = g(q)$ has the two stable fixed points $u = \pm 1$ and the unstable fixed point $q = a$. It is well known, that (1c) has travelling front solutions, e.g., $q(x,y,t) = q_f(x - c_0 t)$, $q_f(\xi) \to \pm 1$ as $\xi \to \pm \infty$, in fact explicitly given by $c_0 = \sqrt{2a}$ and $q_f(\xi) = \tanh(\xi/\sqrt{2})$. For $a < 0$ ($a > 0$) fronts travel left (right), meaning that the +1 phase invades the −1 phase (resp. vice versa).

Since the Laplacian is isotropic any orientation of fronts is allowed. As a consequence, (3) also has (smooth) V-shaped fronts $q_f$, propagating with speed $c_1 = c_0 \sqrt{1 + 1/m^2}$, see Fig. 2 and [19].

FIG. 2: Heuristics for V-shaped fronts of (3).

Now considering the coupling between (1a,1b) and (1c) in more detail we note that $|d_{uu}q\Delta q|$ becomes large near corners of the front, and vanishes away from the front; thus $(u,v)$ excitations originate near corners. On the other hand, the term $-\delta(u - u_\ast)q^2$ in (1a) makes the $(u,v)$ kinetics less excitable away from the front, and thus excitations in the PDE (1) stay near the front. Finally, the term $\gamma(1 - q^2)(u - u_\ast)$ in (1c) has the effect that the excitations push or pull the $q$-front, as seen in the experiment.

System (1) was integrated numerically in a domain $\Omega = [-L, L]^2$ for various parameters using different initial conditions (IC) $(u,v,q)|_{t=0} = (u_0, v_0, q_0)$ and boundary conditions (BC). For the IC we are led by the experiment to consider "wedges" in $q$, e.g.,

$$q_0(x,y) = \begin{cases} 
-1 & x < x_0 - m|y| \\
1 & x \geq x_0 - m|y| 
\end{cases},$$

where $\pm m \in \mathbb{R}$ are the slopes of the sides and $x_0 \in \mathbb{R}$ represents the position of the tip. For $(u,v)$ we choose the fixed point $(u_0, v_0) = (u_\ast, v_\ast)$. Given an IC of the form (4), it is natural to integrate (2) in a moving frame $\xi = x - \eta t$ with $\eta \approx c_1(m)$ to keep the tip of the wedge away from boundaries, i.e., to integrate

$$\partial_t U = f(U) + D\Delta U + \eta \partial_\xi U.$$ 

For the BC the problem then is that while planar fronts can be easily simulated with Neumann BC, for $V$-shaped fronts influences of boundaries on the fronts are difficult to avoid. Here we choose Dirichlet BC for (5), namely

$$(u,v)|_{\partial \Omega} = (u_\ast, v_\ast) \text{ and } q = \pm 1 \text{ on } \xi = \pm L,$$

$$q(\xi, \pm L) = q_f(\xi - \xi_0).$$

The latter fixes the front shape and position at the top and bottom boundary.

For the IC and BC chosen above, we obtain the simulation results displayed in Fig. 3. Excitations nucleate at the tip of the wedge and then travel along the front, pushing it back and forth. The chosen $\gamma = -0.05 < 0$ means that $u > u_\ast$ ($u < u_\ast$) pushes $q$ down (up), such that here the excitations push back the frontline. The firing process at the tip repeats for some time (essentially depending on the size of the computational domain), and the process is accompanied by some overall reshaping of the wedge. Aside from boundary effects, this reshaping is determined by the following factors. The $q$-front does not fully recover its former position after a $(u,v)$ pulse has passed. The tip of the wedge, where pulses nucleate, drifts to the right. To counteract this effect we chose $\eta = 3c_1/4$ (instead of $\eta = c_1$ which without coupling to the $(u,v)$ system would give a stationary tip position). As a consequence of decreasing $|\eta|$, the unperturbed sides of the wedge drift to the left. The overall balance gives an almost stationary average front position up to $t = 500$. For $t > 500$ excitations that have emanated from the tip are reflected by the boundary.

The behaviour in Fig. 3 is quite robust with respect to most parameters and ICs, including the opening angle of the wedge. A decisive parameter for the evolution is $\gamma$. For $\gamma = -0.2$ the excitations push the front too strongly thus destroying the wedge by creating a bubble. For $\gamma = 0.1$ the excitations pull the front too strongly thus flattening the wedge, see Fig. 4.
FIG. 3: Numerical integration of (1) in frame moving with speed \( \eta = 3c_1/4 = -0.15 \). Parameters \( d_u = 0.09, d_v = 0.01, d_{uq} = 0.1, \beta = 0.2, \delta = 0.5, \varepsilon = 0.03, \gamma = -0.05, a = -0.1 \). IC for \( q \) is the wedge (4) with \( x_0 = L/4, m = 1 \), ICs for \((u,v)\) are \((u_s,v_s)\). BC according to (6) with \( \xi_0 = -3L/4 \).

FIG. 4: Same parameters and IC as in Fig.3 except for \( \gamma \).

In summary, we observed excitability in a catalytic surface reaction which remained strictly localized at the interface of two domains of different adsorbates. The excitations were traveling along the interface in a pulse-like way, causing lateral displacements of the interface position. Mechanistically, the localized excitability can be traced back to the diffusive mixing of the two separate adsorbates at the interface causing the formation of a mixed coadsorbate phase which is required to make the system excitable. The experimentally observed behavior could be reproduced with a general dimensionless 3-variable model which couples the excitability of a subsystem to the position of a frontline. The nucleation of excitations at corners of the front was explained with cross-diffusional effects which are very sensitive to the local front geometry. Similar dynamical behavior should be expected in all systems which (i) are essentially bistable in the sense that there are two asymptotically stable phases, but where (ii) diffusive mixing at the interface can locally change the dynamical behavior from bistable to excitable.

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