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ORDER AND CHAOS IN NATURE-PHENOMENA AT SURFACES

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In chemical reaction systems far from thermodynamical equlibrium rate oscillations and chemical wave patterns develop. This paper presents a condensed overview of recent developments in the study of self-organization processes during heterogeneously catalyzed reactions, whereby the main emphasis is focused on low pressure single crystal studies of oscillatory and pattern forming reactions on Pt and Rh surfaces. Chemical wave patterns on a macroscopic scale as well as reaction induced-microscopic roughening and coverage fluctuations in nano-scale systems are discussed.

Keywords: heterogeneous catalysis, kinetic oscillations, spatiotemporal patterns, single crystals
PACC: 8265, 6116, 8220

I. INTRODUCTION

In systems far from thermodynamical equilibrium self-organization can occur leading to structures ordered in space and time.[1] Such structures have been observed in various fields of science ranging from simple systems in physics like the Bénard convection cells in hydrodynamics to complex systems in biology, for example, the oscillatory kinetics of glycolysis, the self-organization of cell populations or the organization in swarms of insects.[2−4] In chemical reaction systems rate oscillations may develop and/or chemical wave patterns can form. The Belousov-Zhabotinkii (BZ) reaction has been considered for a long time a prototype for an oscillatory chemical system. In this system, catalyzed by metal ions, an organic substance is oxidized by bromate in an aqueous solution. The mathematical description of phenomena such as rate oscillation and chemical wave patterns is well established and it has been shown that such phenomena can occur if the underlying equations are non-linear. Consequently, the whole field, comprising not only solutions of reaction-diffusion equations but also the various dissipative structures in physics or biology, has been termed non-linear dynamics. In the past decades the field of non-linear dynamics has developed into an enormously wide discipline.

In recent years, rate oscillations and chemical wave patterns have been very intensely studied on catalytic surfaces.[5−10] These investigations include mainly single crystal studies conducted typically in an UHV (ultrahigh vacuum) environment under low pressure ($p < 10^{-12}$ Pa) conditions[5,6,9,10]. However, a large number of high pressure ($p \approx 10^5$ Pa) experiments with polycrystalline samples have also been carried out under conditions which are no longer isothermal and where mass and heat transport limitations play a significant role.[7,8] With regard to the fact that the basic phenomena have already been discovered with the BZ reaction, the question arises what new can surface studies contribute to the understanding of oscillatory and pattern forming systems.

In contrast to the BZ reaction and its derivatives the chemistry of the oscillatory and pattern forming surface reactions typically is simple. The complexity nevertheless lies in the energetic interactions of the adparticles leading to adsorbate-induced surface phase transitions, island formation and anisotropic diffusion. The main advantage of surface science is that the various surface analytical techniques allow the study of spatial structures over a wide range of length scales from macroscopic patterns all the way down to the atomic resolution. A detailed microscopic picture of the surface processes can thus be obtained which serves as a basis for formulating realistic mathematical models.

While at the beginning rate oscillations and chemical wave patterns were considered as intriguing, if not more or less exotic phenomena, it became increasingly clear that self-organization processes play an important role in heterogeneous catalysis. Self-organization at various length scales may be present even when a stationary reaction rate indicates a seemingly trivial behavior. Attempts to exploit the non-linear characteristics of surface reactions for improving yield and selectivity of catalytic reactions have been made by designing micro-structured surfaces ("microchemical engineering") and by periodic forcing a reaction instead of using constant parameter values. [8,11,12]

Self-organization processes became particularly important in catalytic reactions on nano-scale surfaces since now atomic scale ordering processes came into play. Fluctuation, which arise due to the stochastic nature of the elementary processes of reaction and diffusion, are gaining on importance. For designing nano-scale catalysts the understanding of the dynamics of the reaction on an atomic level will be essential. This includes reaction-induced morphological changes of the catalyst, which proceed rapidly on an atomic scale, as well as diffusion coupling and spillover effects.

In this paper no attempt will be made to give a comprehensive overview of the field of non-linear dynamics in surface reactions and the reader is referred here to several review papers and monographs on this subject.[5−10] Instead, the main directions and, in particular, the connection to nano-scale systems will be illustrated here with a few selected examples.

II. RATE OSCILLATIONS IN CATALYTIC REACTIONS

Rate oscillations in catalytic reactions have first been discovered by the research group of Wicke about thirty years ago.[13] Catalytic CO oxidation is still the most widely studied oscillatory reaction but oscillatory behavior has also been found in many other catalytic reactions, and it has been even speculated that in a certain parameter range any catalytic reaction will probably exhibit oscillatory behavior.[8] The experimental studies can be grouped into two types, i.e. high pressure experiments (10^{-1} Pa $< p < 10^5$ Pa), which are typically conducted with polycrystalline materials under non-isothermal conditions, and single crystal studies, carried out under isothermal low pressure conditions ($p < 10^{-1}$ Pa). Quite early, a periodic oxidation and reduction of the catalyst as cause for the periodic changes in catalytic activity during catalytic CO oxidation has been suspected for experiments conducted at atmospheric pressure.[7,8] Experimentally proven mechanisms could, however, only be established when studies on a single crystal were carried out, allowing an *in-situ* control of the state of the catalyst surface under oscillating conditions and ruling out the influence of contaminants. In these single crystal studies reactions of the automotive catalytic converter, i.e. catalytic CO oxidation and catalytic NO reduction, were investigated on various Pt, Pd, and Rh single crystal planes.[5,9,10] An example of rate oscillations in catalytic CO oxidation on a Pt(110) surface is displayed in Fig.1.

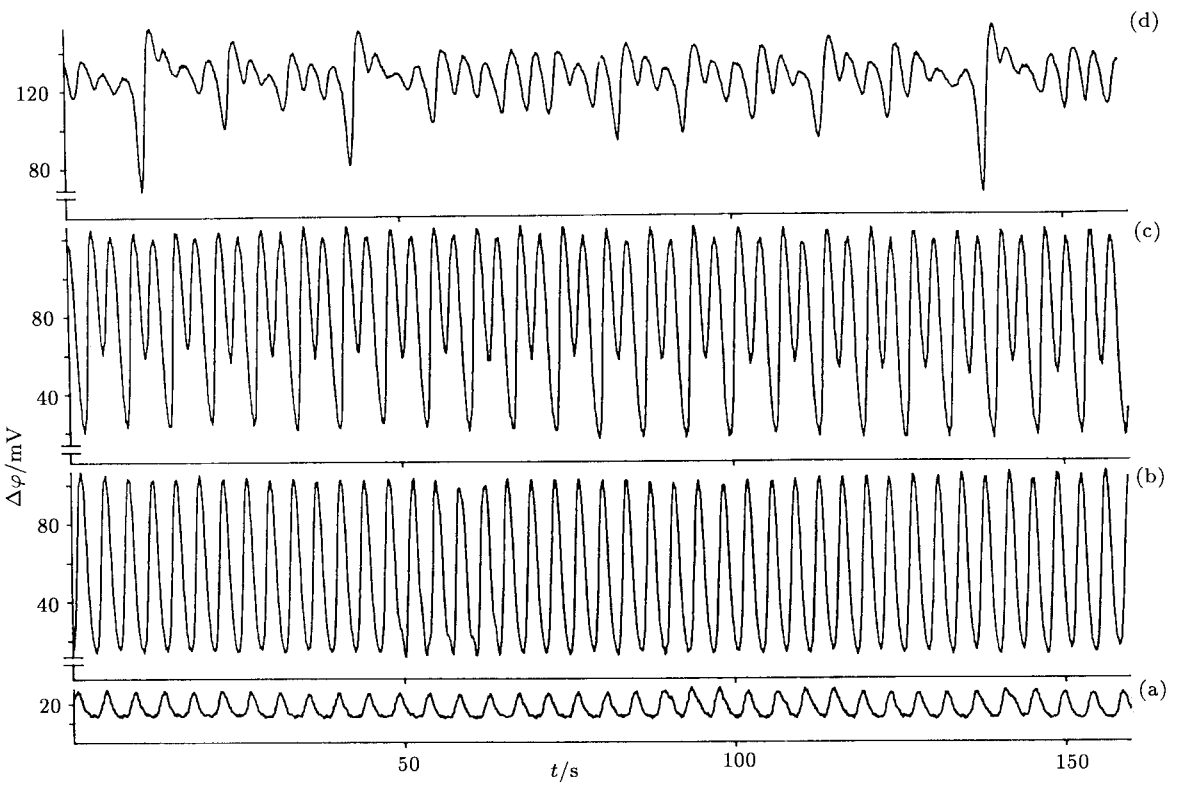


Fig.1. Development of kinetic oscillations and transition to chaotic behavior via period-doubling as p_{CO} is varied as bifurcation parameter in catalytic CO oxidation on Pt(110). Depicted is the variation of the work function, which has been shown to be proportional to the CO_2 production rate. Experimental conditions: $T = 530\ K, p_{O_2} = 8 \times 10^{-3}$ Pa, p_{CO} var. (From Ref.[6]).

Three basic oscillatory mechanisms were found[5,9]:

a) Reversible structural changes of the surface for catalytic CO oxidation on Pt.

The clean Pt(100) and Pt(110) surfaces exhibit a quasi-hexagonal ("hex") and 1×2 "missing row" reconstruction, respectively, which can be reversibly lifted by adsorbed CO thereby constituting an adsorbate-induced surface phase transition. Under oscillatory conditions the surface switches periodically between the two configurations, and the change in the catalytic activity caused by the difference in the oxygen sticking coefficient of the two phases gives rise to oscillations in the reaction rate. On high-index planes of Pt this principle is modified to include reversible facetting as structural changes causing rate oscillations.

b) Reversible formation of subsurface oxygen for catalytic CO oxidation on Pd surfaces.

At sufficiently high oxygen partial pressure chemisorbed oxygen can penetrate reversibly into the Pd bulk forming subsurface oxygen which changes the catalytic activity. This mechanism is closely related to the oxidation-reduction mechanism proposed for atmospheric pressure experiments.

c) The vacancy model for catalytic NO reduction on Pt(100) and on Rh surfaces.

Catalytic NO reduction with CO, H_2 or NH_3 as reducing agent proceeds via dissociation of molecularly adsorbed NO. The vacant site requirement for NO dissociation constitutes an autocatalytic behavior which represents the essential element of the oscillation mechanism.

The different mechanisms have been cast into mathematical models with which the experimental findings could very well be reproduced. It should be added that more detailed experimental studies revealed that in practice the division into different mechanistic schemes is not as clear cut as sketched above. As an example, on Pt surfaces also subsurface oxygen is formed and it was demonstrated that this species can decisively influence the dynamic behavior of the reaction.[14]

III. SPATIOTEMPORAL PATTERNS

A. Local and global coupling

In order to produce macroscopic rate oscillations it is not sufficient to have an oscillation mechanism, but the different local oscillators on the surface need to be synchronized by a coupling mechanism. This coupling can be provided by (i) surface diffusion of a mobile adsorbate, (ii) through the gas phase via the partial pressure changes that arise due to mass balance in the reaction, and at high pressure by (iii) thermal coupling through the exothermicity of the reaction. While surface diffusion represents a local coupling, coupling via the gas phase is global in nature since all parts of the surface are affected in the same way and (at low p) without noticeable delay. A completely synchronized oscillating surface may therefore result on which all changes take place spatially uniformly. In the absence of global coupling only surface diffusion is present as coupling mechanism at low pressure and one obtains various chemical wave patterns similar to the well known patterns observed with the BZ reaction in aqueous solution. Interesting cases result, when both coupling mechanisms, gas-phase and surface diffusion, compete. In that case one may observe new types of patterns not known in the liquid phase such as standing waves or cellular structures, or incomplete synchronization may lead to the appearance of chaotic behavior.[9,15,16]

B. Chemical wave patterns

Coupling of a reaction with diffusion can lead to simple reaction fronts in bistable media as well as to pulses forming rotating spiral waves or target patterns in the case of excitable media.[4] Under certain conditions irregular patterns may develop, leading to chemical turbulence, where a disordered state is reached, which bears some similarities to turbulence in hydrodynamics. The various types of chemical wave patterns are, of course, well known from the BZ reaction, but on catalytic surfaces several principal differences exist with respect to the liquid phase:

a) Surface diffusion is in general anisotropic and the diffusion constants of the various surface species can vary over many orders of magnitude as compared to the liquid phase, where diffusion is isotropic and all species diffuse approximately equally fast.

b) In addition to diffusive coupling, also global coupling via the gas-phase is present, leading to standing wave patterns and cellular structures, as observed for $Pt(110)/CO+O_2$.[6,16]

c) Energetic interactions between the adparticles lead to the formation of ordered structures and non-Fickian diffusion. The diffusion flux no longer follows the gradient in the concentration but in the chemical potential. So-called "up hill" diffusion can be ob-

served; nearly atomically sharp reaction fronts have been seen in atomic-scale experiments.[17,18]

Spatiotemporal pattern formation has been extensively investigated in catalytic CO oxidation on Pt(110).[6] In addition to the above mentioned patterns travelling oxygen pulses, exhibiting under certain conditions soliton-like behavior, have been observed.

In the system Rh(110)/NO+H_2 atomic oxygen and nitrogen cause surface reconstructions with different anisotropies and consequently the diffusion anisotropy becomes state-dependent.[19,20] This feature allows the formation of new types of patterns, which are not possible in the liquid phase, such as wave fragments travelling along certain crystallographic directions as well as the formation of rectangularly shaped patterns, as demonstrated by the spiral wave shown in Fig.2.

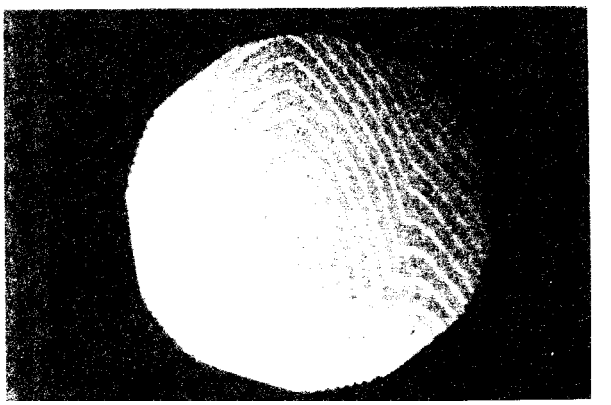


Fig.2. PEEM image of the NO+H_2 reaction on Rh(110) showing a rectangularly shaped spiral wave in a medium with state-dependent anisotropy. Experimental conditions:T=620 K, p_{NO}=1.8×10^{-4} Pa, p_{H_2} = 5 × 10^{-4} Pa; the diameter of the imaged area is 400 μm.

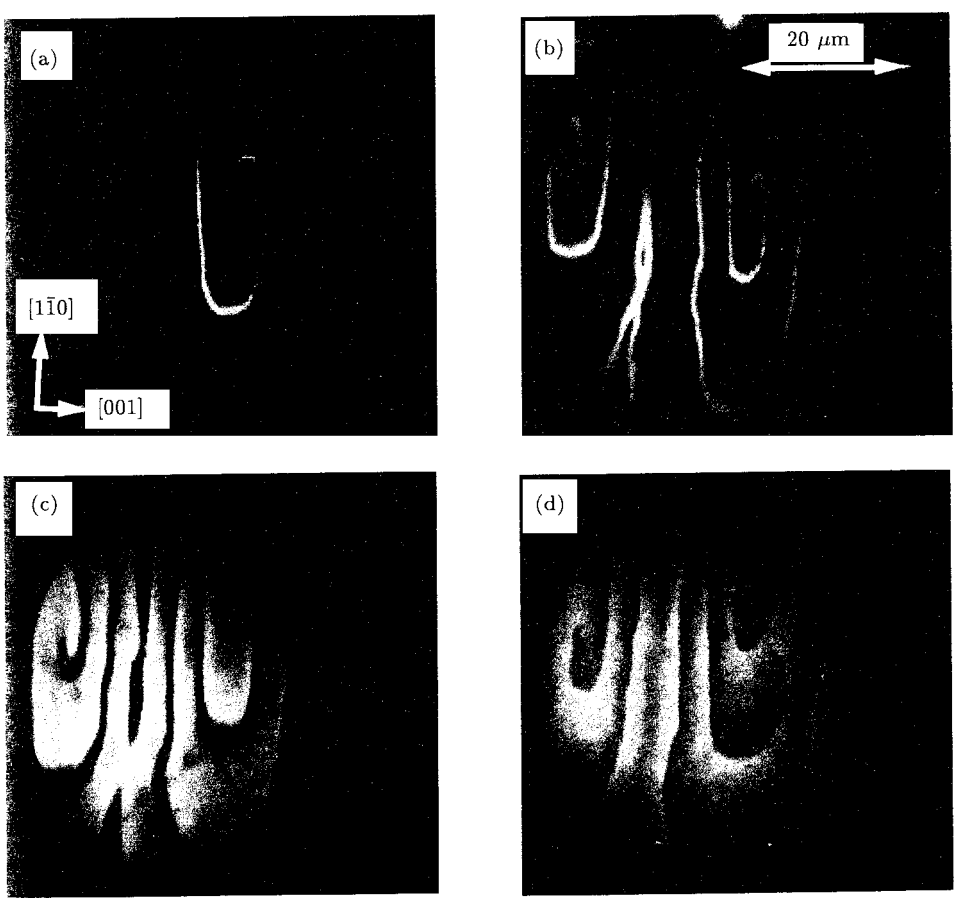


Fig.3. Dark field images of a spiral wave on Rh(110) with LEEM, showing the existence of various ordered reconstruction phases in a chemical wave. The various reconstruction phases can be assigned to different states in the excitation cycle of a pulse. The images were taken approximate 1 min apart. Experimental conditions: T =550 K, p_{NO}=3.5× 10^{-5} Pa, p_{H_2}=2 × 10^{-4} Pa. (From Ref.[23]). (a) (3 × 1)-N=excited state I, (b) (2× 1)-N=excited state II, (c) c(2 × 4)-2, N=refractory phase, (d) c(2 × 6)-O=resting state.

The most widely used spatially resolving technique for imaging chemical wave patterns is photoelectron emission microscopy (PEEM), which is based on the dependence of the yield of the photoelectrons on the local work function.[21] PEEM therefore yields no or only indirect information about the chemical identity of the imaged species and no information about structural changes of the surface as well. For chemically more complex systems like Rh(110)/NO+H_2, scanning photoelectron microscopy (SPEM), which utilizes synchrotron radiation to image the specific core levels of elements, is available.[22] A method, which is based on diffraction contrast, is low energy electron microscopy (LEEM), which images ordered structures and is sensitive to structural changes of the substrate.[16,23] Figure 3 displays LEEM images of a spiral wave in Rh(110)/NO+H_2 showing a sequence of several ordered N, O-phases in a pulse.[23]

C. Reaction-induced substrate changes

All catalytic reactions modify, to a certain extent, the substrate, which may often lead to real morphological changes. In Pt(110)/CO+O_2 the CO-induced $1\times1 \leftrightarrow 1 \times 2$ phase transition is associated with a mass transport of 50% of the surface atoms. As a consequence rate oscillations associated with the $1\times1 \leftrightarrow 1\times2$ phase transition cause a certain roughening of the surface which may even turn into a (micro) facetting.[24] This roughening/facetting is reversible, therefore becoming a part of the pattern forming surface processes. LEEM images demonstrating the formation of channel-like structures on a Pt(110) surface roughened by catalytic CO oxidation are displayed in Fig.4.[25] Inside the channels formed by roughened Pt

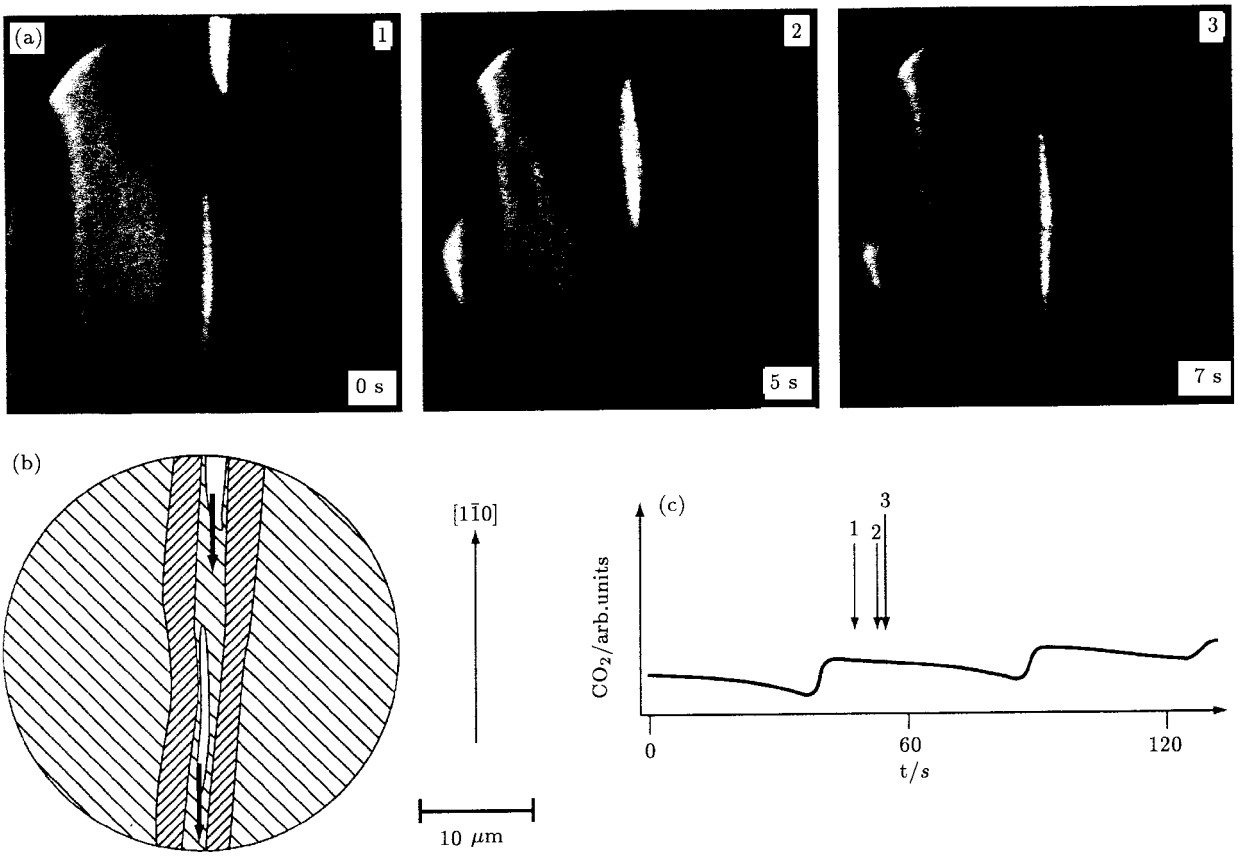


Fig.4. LEEM images demonstrating the formation of a channel structure on the roughened Pt(110) surface during rate oscillations. Experimental conditions: T =430 K, p_{CO}=5×10^{-4} Pa, p_{O_2} =9.9 × 10^{-4} Pa. (From Ref.[25]). (a) LEEM images showing the propagation of oxygen pulses (bright elongated areas) along a single channel on each side; the two dark stripes in the center are roughened CO-covered areas. Dark and light regions in the area outside the channel mark CO-and oxygen-covered surfaces, respectively. (b) Schematic drawing of the LEEM images in (a), in which the roughened and flat areas of the surface are indicated by different shading. Oxygen pulses move inside the channel. (c) Rate oscillations corresponding to the images in (a). Arrows mark the points where the images were taken.

(110) surface oxygen pulses (bright areas) propagate, while in between the channels CO covered surface area periodically expands and contracts, forming a standing wave pattern. The reversible roughening/facetting effectively introduces an additional slow time scale into the dynamics of the system, giving rise to the formation of rather complex patterns.

IV. ATOMIC SCALE EXPERIMENTS

Scanning tunneling microscopy (STM) is a technique which, in principle, allows for the *in-situ* imaging of catalytic surface reactions. Due to inherent problems (influence of the electric field between tip and surface on the adsorbate, shielding effect of the tip on the impinging gas particles) as well as due to technical problems (thermal drift of the sample), this method has so far only been applied to titration experiments. In the titration of an oxygen Pt(111) surface with hydrogen for the first time a reaction front could be imaged with atomic resolution.[18] A very old technique, yielding with $\sim$ 2 nm nearly atomic resolution, is field electron microscopy (FEM). With this technique a number of oscillatory reactions could be imaged *in-situ* on Pt and Rh field emitter tips.[26,27] Nearly atomically sharp interfaces in the O_2+H_2 reaction on a Pt tip could be observed with the better resolving (about 0.2-0.3 nm) field ion microscopy (FIM).[17] However, for this method the strong influence of the electric field is a severe problem. To a smaller extent this is also true for the FEM method but, at least for catalytic CO oxidation, the effect of the electric field was shown to be negligibly small.[28] In an area of approximate 2 nm diameter, which is the resolution of FEM, only a few hundred adparticles are present. This means that fluctuations in the density of adsorbed particles, which arise due to the stochastic nature of the elementary processes, now become accessible to observation. These fluctuations may lead to a departure from the predictions of macroscopic (mean field) rate laws. For example for bistable systems, fluctuation-induced transitions between the two macroscopically stalbe branches of a reaction have been predicted. Figs.5 and 6 demonstrate the experimental observation of such fluctuation-induced transitions in catalytic CO oxidation on the (110) facet of a Pt tip.[29] In Fig.5 the FIM and FEM images of a Pt tip are depicted and the diagram in Fig.6 shows fluctuations of the lcoal FEM brightness recorded under different reaction conditons from a 2 nm $\times$ 2 nm area on the Pt tip in Fig.5. The bimodal amplitude distribution, which was observed for the bistable range, can be considered as evidence for fluctuation-induced transitions since the system spends most of its time on either of the two branches, and comparatively little time in between.

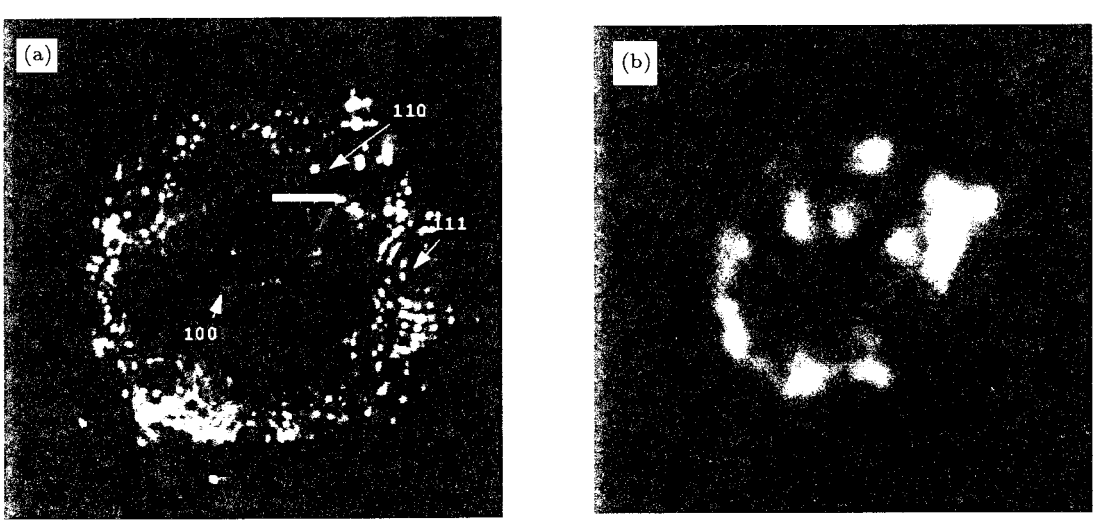


Fig.5. Catalytic CO oxidation on a Pt field emitter tip. (a) FIM image showing the crystallography of the Pt tip (T=78 K, imaging gas Ne, field strength F=36 V/nm). The rectangular window indicates the area in which fluctuations were studied. (b) FEM image of the same area (same scale) shown in (a) under reaction conditions (T=310 K, p_{O_2} =5.3$\times 10^{-2}$ Pa, p_{CO}=5.3 $\times$ 10^{-5} Pa, F=4 V/nm).

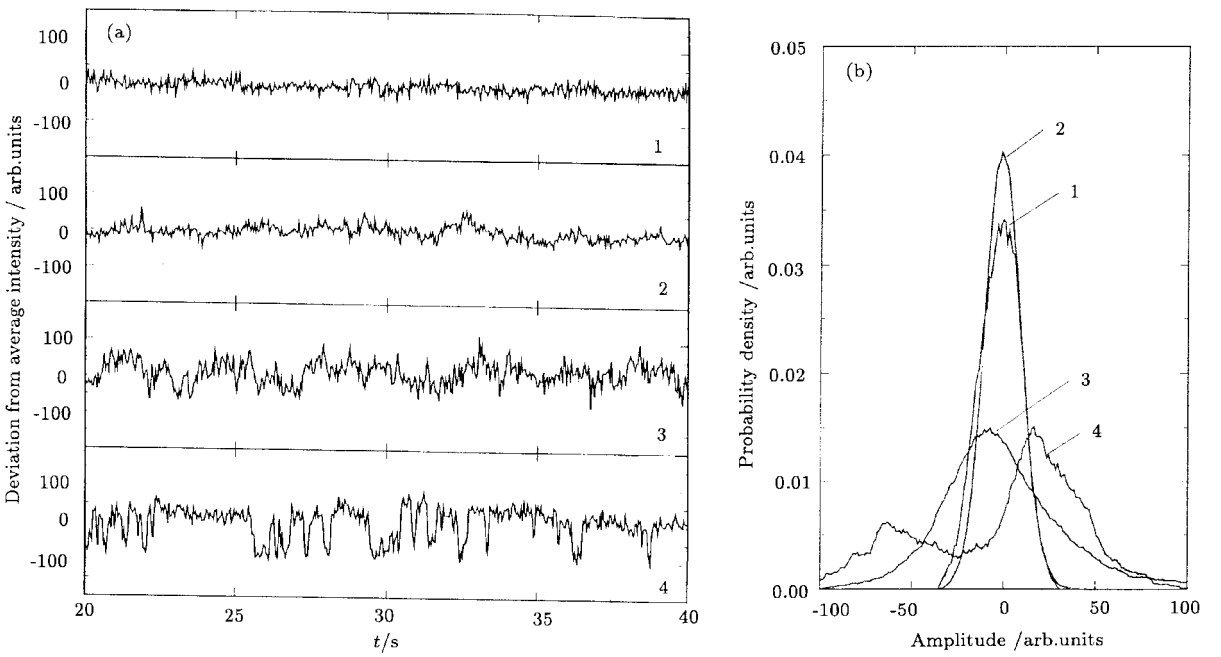


Fig.6. Fluctuations in catalytic CO oxidation on a Pt field emitter tip under different reaction conditions (T=310 K, p_{O_2}=5.3 × 10^{-2} Pa, p_{CO} = 5.3 × 10^{-5} Pa, F=4 V/nm). (From Ref.[29]). (a) Time series of the local (2 nm×2 nm) FEM brightness in the area marked in Fig.5(a). (b) Probability distributions corresponding to the time series shown in (a).

V. PRESSURE AND MATERIAL GAP PROBLEM

The huge difference in pressure range and in materials between UHV single crystal experiments and the so-called "real catalysis" is known as the pressure gap and material gap problem in heterogeneous catalysis, respectively. A similar problem exists if one tries to extrapolate the mechanisms found in low pressure single crystal experiments to oscillatory systems at atmospheric pressure. A very successful attempt to bridge the pressure gap in catalytic CO oxidation has been achieved with the introduction of optical techniques, as threre are ellipso-microscopy (EMSI) and reflection anisotropy microscopy (RAM), to image chemical wave patterns at high pressure (p >100 Pa).[30] As an attempt to bridge the material gap for bimetallic catalysts we can consider the design of micro-structured bimetallic catalysts on which diffusion coupling effects were investigated with PEEM and SPEM.[12]

VI. OUTLOOK

Over the past two decades a very good understanding of the various self-organization phenomena has been reached. The main challenges now are to bridge the pressure as well as the material gap between single crystal studies and real catalysis and to develop a better understanding of the dynamic processes on an atomic scale. Only very few studies exist, covering the range between 1 μm and 0.1 nm, but this is exactly the range which will be important for controlling catalytic reactions through the design of nano-scale catalysts.

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