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Regular and irregular spatial patterns in the catalytic reduction of NO with NH_3 on Pt(100)

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The catalytic reduction of NO with NH_3 on a Pt(100) surface, which exhibits kinetic oscillations under isothermal conditions in the 10^{-6} mbar pressure range, has been studied by photoemission electron microscopy (PEEM) as a spatially resolved technique. Oscillations in the rate of product formation for N_2 and H_2O are observed between 425 and 450 K. During the rate oscillations, the surface reacts predominantly spatially uniformly. Towards the lower T-boundary for oscillations, however, fluctuating adsorbate islands (diameter $\approx$ 10–50 μm) appear and one observes target patterns and rotating spirals. Below the lower T-boundary for oscillations, the reaction rate is stationary, but with PEEM one observes a spatially chaotic pattern in which the surface is still oscillating locally. The transition from macroscopic rate oscillations to unsynchronized oscillatory behavior can be associated with the breakdown of long range synchronization via gas phase coupling. In the spatial patterns imaged by PEEM, one can clearly identify three distinct grey levels which undergo a cyclic transformation into each other via propagating reaction fronts. One can assign different mechanistic steps to these transformations, namely the lifting of the hex reconstruction through NO adsorption and the dissociation of NO on the 1×1 phase, decomposition of NH_3 on the 1×1 O_{ad}/NO_{add} phase, and the restoration of the hex surface.

Keywords: Catalytic NO reduction; kinetic oscillations; spatial pattern formation; chemical turbulence

1. Introduction

Spatially resolved measurements during kinetic oscillations have revealed that the variations in the reaction rate are associated with spatially and temporally varying concentration patterns on the catalyst surface [1,2]. Most of these investigations have been performed under isothermal conditions at low pressure ($p < 10^{-3}$ mbar) on single crystal surfaces where the newly developed photoemission electron microscope (PEEM) demonstrated a spectacular variety of different spatiotemporal patterns [3–5]. In this paper, we report the results of PEEM measurements in the $NO + NH_3$ reaction on Pt(100) whose oscillatory behavior has been investigated earlier [6–8].

This work is part of an ongoing investigation in which we have studied the oscillatory behavior of the NO reduction with the reactants CO [5,9], H_2 [10] and NH_3 [6,7] on a Pt(100) surface at low pressure (10^{-6} mbar). All these systems exhibit similar dynamical behavior whose origin presumably lies in the requirement of vacant sites for NO dissociation which is the rate-limiting reaction step:

$$NO_{ad} + * \rightarrow N_{ad} + O_{ad},$$

where $*$ denotes a vacant site. Since more vacant sites are liberated in the subsequent product forming steps than are consumed by the above step, autocatalytic behavior results. In all three NO + X reactions (X = CO, H_2, NH_3) on Pt(100), the autocatalysis manifests itself by the occurrence of extremely narrow product peaks at $T \approx 400$ K in temperature programmed reaction (TPR) studies [11,12]. This effect has been referred to as "surface explosion".

Although one can suspect that in the NO + NH_3 reaction the "surface explosion" plays a similar key role in the oscillatory mechanism as in the NO + CO reaction, which has been analyzed in depth previously [9,12], the picture is rather complicated in the present case. As will be shown in this report, in PEEM we observe spatial patterns with a characteristic sequence of transformations which we can associate with different steps of the overall mechanism. Thus, the results of spatially resolved measurements can help to clarify a complicated catalytic mechanism.

2. Experimental

The experiments were conducted in a standard UHV system of 80 ℓ volume which was operated as a gradient free flow reactor, continuously pumped by a 360 ℓ/s turbomolecular pump (effective pumping rate ≈ 100 ℓ/s). For rate measurements, a differentially pumped quadrupole mass spectrometer (QMS) was attached to the chamber. During PEEM measurements, UV light from a deuterium discharge lamp with a maximum emission between 5.2 and 6.2 eV photon energy was focussed onto the sample into a small spot (≈ 1 mm^2) [13]. The emitted photoelectrons from the sample were focussed by the electrostatic three lens system of the PEEM, amplified by a channel-plate electron multiplier, and then imaged onto a phosphorous screen. These images were then recorded with a CCD camera and stored on a video tape. The Pt(100) sample, which was of the dimensions $\approx 5 \times 5$ mm^2 and ≈ 1 mm thickness, was cleaned by standard methods involving repeated cycles of oxidation and Ar ion sputtering. For the experiments, high purity gases were used (NO 99.8%, NH_3 99.7%) which were introduced into the chamber via leak valves. All PEEM images shown were recorded with the same magnification such that the width of the imaged area is about 450 μm. The vertical and horizontal axes in the PEEM pictures are aligned with the vectors of the square substrate lattice.

3. Results

The $NO + NH_3$ reaction on Pt surfaces yields as main products N_2 and H_2O according to

$$6\ NO + 4\ NH_3 \rightarrow 6\ H_2O + 5\ N_2 .$$

The clean Pt(100) surface exhibits a quasihexagonal reconstruction (hex) which can be reversibly lifted upon NO adsorption [12,14]. Thus, an adsorbate-induced $1 \times 1 \rightleftharpoons$ hex phase transition exists which controls the catalytic activity of the surface, since only the bulk-like 1×1 surface phase is efficient in dissociating NO [14]. Neglecting the formation of intermediates (NH_x, $x = 1$–3), the catalytic $NO + NH_3$ reaction can be described by the following sequence of steps ($*$ denotes a free absorption site):

$$NO + * \rightleftharpoons NO_{ad}, \tag{R1}$$

$$NH_3 + * \rightleftharpoons NH_{3,ad}, \tag{R2}$$

$$NO_{ad} + * \rightarrow N_{ad} + O_{ad}, \tag{R3}$$

$$NH_{3,ad} + 3* \rightleftharpoons N_{ad} + 3\ H_{ad}, \tag{R4}$$

$$2\ N_{ad} \rightarrow N_2 + 2*, \tag{R5}$$

$$O_{ad} + 2\ H_{ad} \rightarrow H_2O + 3*. \tag{R6}$$

As one heats and cools a Pt(100) sample in an atmosphere of NO and NH_3, one observes a complicated hysteresis in the reaction rate and in the surface structure which is depicted in fig. 1a and which has been discussed in detail earlier [6]. Above the temperature of the "surface explosion" between 420 and 440 K (depending on p_{NO}), the surface remains in a state of high activity until with decreasing adsorbate coverages the surface transforms into its inactive "hex" configuration. Upon cooling, the NO induced lifting of the hex reconstruction restores the state of high catalytic activity. During this transition from low to high reactivity, kinetic oscillations are found in a temperature interval of 15–20 K width as indicated by the solid bar in fig. 1a. The steady state behavior as well as the kinetic oscillations in the $NO + NH_3$ reaction are almost identical to that of the $NO + H_2$ reaction on Pt(100), indicating that the source of the hydrogen atoms plays no important role [7].

As one traverses the cooling branch of the rate hysteresis with PEEM, one observes a variety of different spatiotemporal patterns which shall be described in the following. When the sample is cooled to the temperature at which oscillations first occur, the intensity of the PEEM picture varies homogeneously

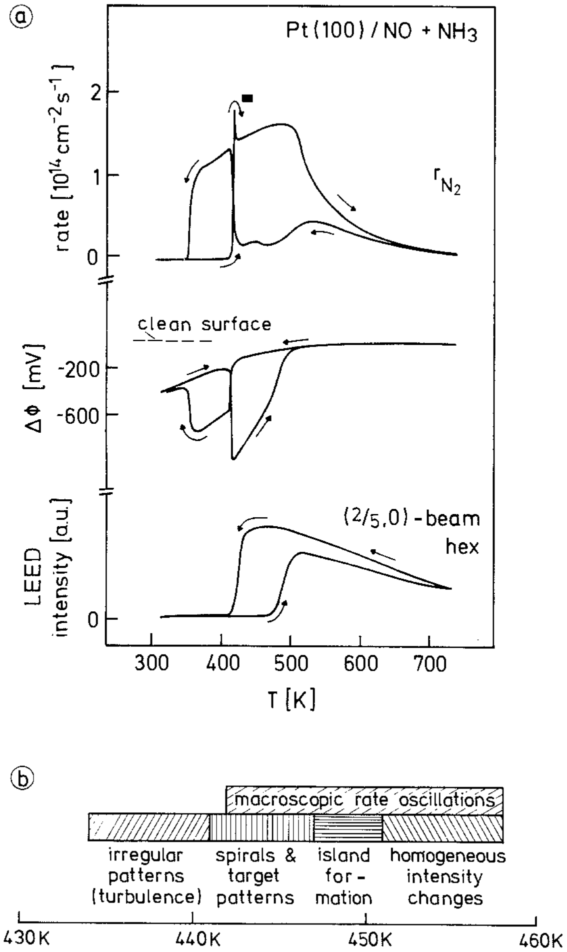

Fig. 1. (a) Hysteresis in the N_2 production rate, the work function and the hex LEED-beam intensity as the temperature is slowly varied in a cycle with constant educt pressures ($p_{NO} = 1.1 \times 10^{-6}$ mbar, $p_{NH_3} = 1.6 \times 10^{-6}$ mbar). The solid bar indicates the temperature range in which macroscopic rate oscillations were observed in the cooling branch of the hysteresis (adapted from ref. [6]). (b) Schematic overview of the temperature ranges in which macroscopic rate oscillations and different pattern formation on the catalyst surface take place. The partial pressures of the reactants were $p_{NO} = 2.1 \times 10^{-6}$ mbar and $p_{NH_3} = 5.6 \times 10^{-6}$ mbar.

with the changes in the reaction rate. The intensity variations are just detectable by eye so one can assume that the adsorbate coverage always remains low during the oscillations. The phase relationship between the rate oscillations and the changes seen in PEEM are such that the dark grey level coincides with the rate minimum, while the bright grey is associated with the rate maximum.

Since the surface is oscillating homogeneously, synchronization of the different local oscillators is evidently achieved via gas phase coupling. The oscillations react extremely sensitively to small variations of p_{NO} (a variation in the order of a few ‰ leads to detectable changes), which leads us to the conclusion, that gas phase coupling is accomplished by changes in p_{NO}. These changes are in the order of $\approx 1\%$ and arise as a consequence of mass balance in the reaction.

As one lowers the temperature further to $T = 440$–450 K, islands nucleate, grow to a size of typically 10–50 μm and then dissolve. While the islands are forming, the surrounding area is still oscillating homogeneously. A typical sequence of PEEM images is displayed in fig. 2. The islands form as dark regions which slowly expand ($v_F \approx 0.5$ μm/s) over the grey background. The dark front of the islands is then followed by an expanding bright zone which advances more rapidly ($v_F \approx 1.1$ μm/s) than the outer dark zone. As a consequence of the difference in velocities, the bright area overruns the dark front and extinguishes the island growth. The brightness of the remaining area then gradually decreases until it is back at the grey level of the hex surface. This latter process therefore causes the disappearance of the whole island.

The interpretation of the different grey levels in the PEEM images can be made in a straightforward way with the help of fig. 1a and the results of earlier investigations [5,12]. The only two species which are present in this system in large concentrations and which cause a strong change in the work function are adsorbed oxygen O_{ad}, resulting from the dissociation of NO (R3) and adsorbed NH_3 along with its intermediate decomposition products NH_x ($x = 1$–3). The different adsorbates are concentrated on the 1×1 surface while the hex surface can be considered to be practically adsorbate free.

While molecularly adsorbed NO produces only a slight $\Delta\phi$ change of -50 mV, the atomic oxygen which is formed through NO dissociation at $T \geqslant 380$ K can cause a $\Delta\phi$ increase up to 400 mV [12]. The dark area in the PEEM images can therefore be assigned to partially dissociated NO, e.g. to a 1×1-O_{ad}/NO_{ad} phase. The large $\Delta\phi$ decrease of -700 mV which is seen in the $\Delta\phi$ trace of fig. 1a, can be attributed to the presence of a NH_x ($x = 1$–3) species on a 1×1 substrate [6,7,15]. Since the reaction products N_2 and H_2O desorb so rapidly at $T \approx 400$ K that their surface concentration is negligible, the bright area in the PEEM images can be assigned to adsorbed NH_x ($x = 1$–3), probably coadsorbed with some O_{ad}/NO_{ad}.

With these assignments, the patterns seen in the PEEM images in fig. 2 can also be explained quite easily by means of a three step mechanism:

(1) The initial stage of the formation of a dark island on a grey background can be associated with the lifting of the hex reconstruction (grey area) through adsorption of NO. Thus, a growing 1×1 island is created in which part of the adsorbed NO dissociates (step (R3)), thereby forming a mixed NO_{ad}/O_{ad} phase (dark area).

(2) In the 1×1-NO_{ad}/O_{ad} phase NH_3 can adsorb and decompose (steps (R2) and (R4)). The hydrogen reacts off with O_{ad} to form H_2O (step (R6)), thereby replacing the NO_{ad}/O_{ad} layer by NH_x ($x = 1$–3). Since the NH_x species causes a strong $\Delta\phi$ decrease (see fig. 1), this transition shows up in PEEM as the formation of a bright zone.

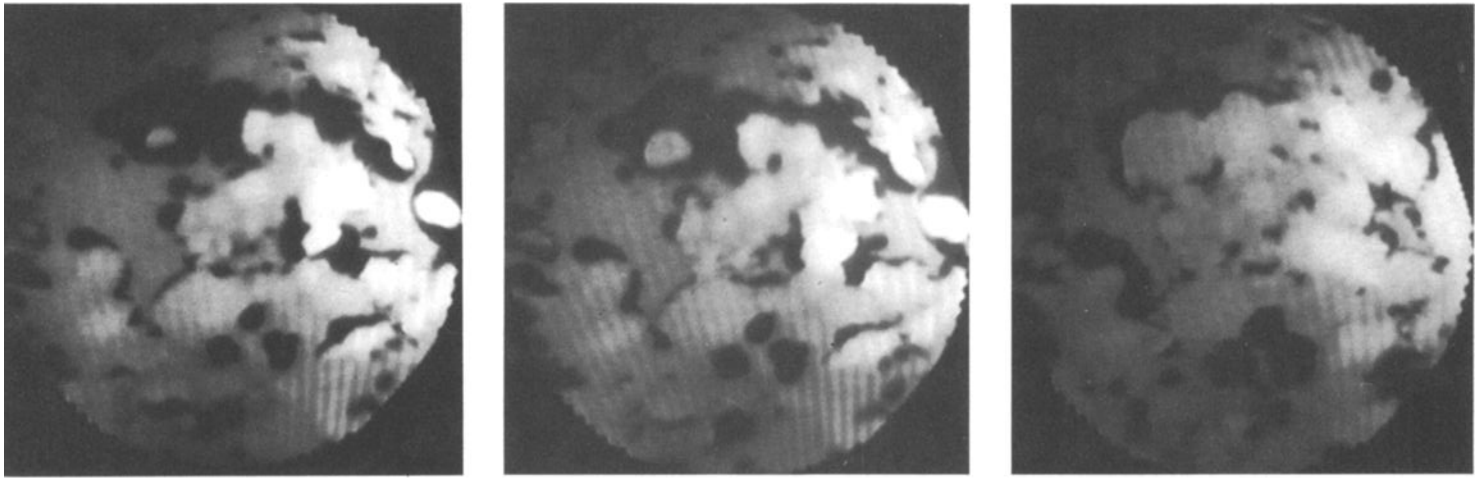

Fig. 2. Sequence of PEEM images showing the formation and extinction of 1 × 1 adsorbate islands on the catalyst surface. In the upper half of the pictures one can follow the extinction of a dark NO_{ad}/O_{ad} island by a bright reaction front which advances more rapidly than the dark/grey front. The pictures were taken with 25 s time delay. The experimental conditions were: $p_{NO} = 1.3 \times 10^{-6}$ mbar, $p_{NH_3} = 2.1 \times 10^{-6}$ mbar and $T = 438$ K.

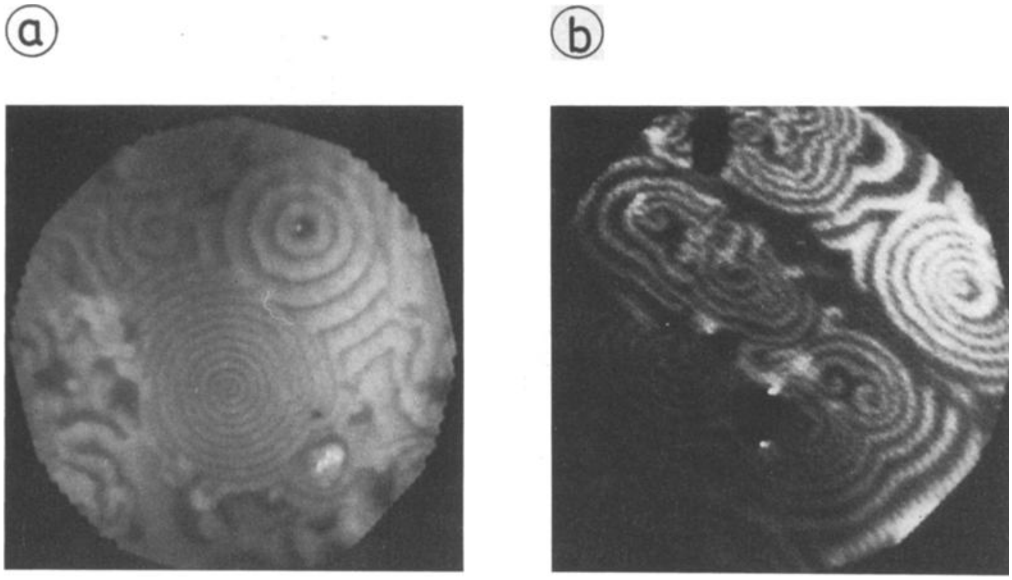

Fig. 3. (a) PEEM image of a spiral coexisting with a target pattern. In the center of the target pattern one recognizes a bright spot, apparently representing a surface defect. The experimental conditions were: $p_{NO} = 2.1 \times 10^{-6}$ mbar, $p_{NH_3} = 5.6 \times 10^{-6}$ mbar and $T = 445$ K. (b) PEEM image showing coexisting spirals and double spirals on the catalyst surface. The experimental conditions were $p_{NO} = 2.3 \times 10^{-6}$ mbar, $p_{NH_3} = 2.8 \times 10^{-6}$ mbar and $T = 450$ K.

(3) The NH_x adlayer which is obtained after step 2 cannot stabilize the 1×1 phase which relaxes back into the inactive hex phase.

The mechanism suggested above is consistent with the hysteresis data shown in fig. 1. These demonstrate that the oscillations take place during the onset of the lifting of the hex reconstruction under conditions where the NH_x coverage is still rather low, as indicated by the $\Delta\phi$ trace. In adsorption experiments with pure NO and pure NH_3, it has been shown that only NO but not NH_3 can lift the hex reconstruction under the reaction conditions. Consequently, in PEEM one does not observe a direct transition from grey to bright which would correspond to this latter process, but only a transition from grey to dark. This observation is thus consistent with the results of the adsorption experiments.

Upon further lowering of the temperature, the fluctuating islands turn into more stable structures, and one observes spirals, rotating with an angular velocity $\omega \approx 1.2$ min^{-1}, and target patterns, in which wave fronts constantly emanate from the same points on the surface (see fig. 3). Both the target patterns and the spirals persist quite independently of the surrounding area on which one may observe either periodic oscillations in phase with the oscillations in the reaction rate or propagating reaction fronts which pass the spirals and target patterns without interfering with them. In some cases, the trigger center of a target pattern, from where all wave fronts emanate, or the core of a spiral,

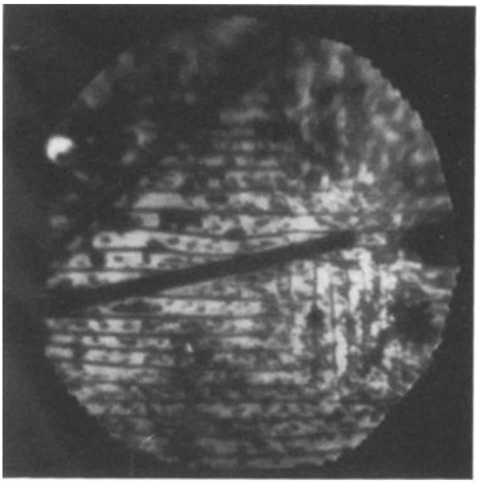

Fig. 4. PEEM image demonstrating that the $NO+NH_3$ reaction can be used to decorate surface defects on Pt(100). The horizontal and vertical dark stripes presumably represent boundaries between the two rotational hex domains of the reconstructed Pt(100) surface. The two large black stripes in the picture are scratches on the crystal surface. The experimental conditions were: $p_{NO} = 1.4 \times 10^{-6}$ mbar, $p_{NH_3} = 4.6 \times 10^{-6}$ mbar and $T = 444$ K.

around which the spiral rotates, is clearly identifiable as a surface defect, but in other cases no such assignment can be made.

Since defect sites can act as nucleation centers for reaction fronts, one may also observe a kind of decoration effect in which the reaction images the domain structure on the reconstructed surface: The horizontal and vertical dark lines

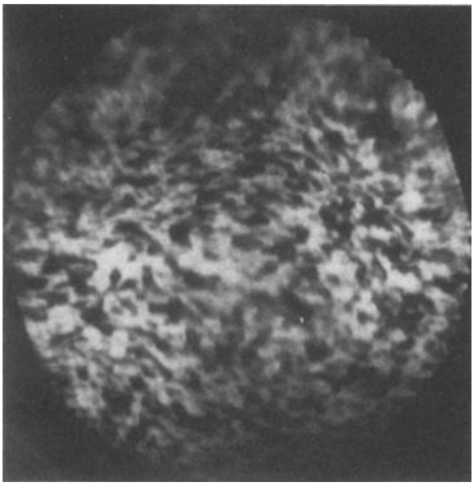

Fig. 5. PEEM image showing irregular spatiotemporal patterns on the catalyst surface with reactant pressures being $p_{NO} = 1.3 \times 10^{-6}$ mbar and $p_{NH_3} = 2.1 \times 10^{-6}$ mbar and temperature $T = 432$ K.

which are visible in fig. 4 presumably represent boundaries between the two possible domain orientations of the hex reconstruction which are perpendicular to each other and aligned parallel to the crystallographic axes.

Below $T = 430$–440 K, the macroscopic rate oscillations disappear and the reaction rate returns to a stationary value. In PEEM, however, one still finds spatiotemporal patterns, but these appear to be completely irregular, as demon-

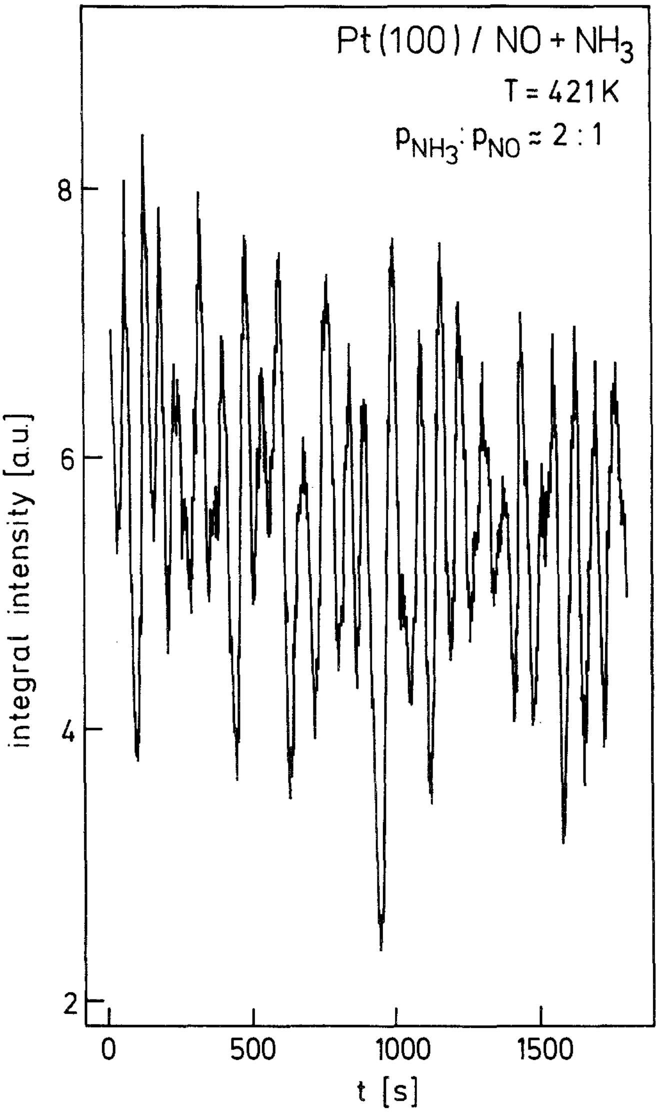

Fig. 6. Time series of the integral intensity of an area of ≈ 30×30 μm from a video sequence of turbulent, irregular PEEM images like the one shown in fig. 5. The local reaction rate, which is proportional to the intensity, exhibits temporal oscillations while the overall reaction rate is stationary. The experimental conditions were: $p_{NO} = 1.2 \times 10^{-6}$ mbar, $p_{NH_3} = 2.6 \times 10^{-6}$ mbar and $T = 421$ K.

strated by the example displayed in fig. 5. By integrating the intensity in a small window and following its time dependent variation, one can see that the surface is still locally oscillating with a high degree of regularity with respect to the frequency, while the amplitude of the oscillations undergoes wild fluctuations. Such a plot, whose data were taken from an arbitrarily positioned window of 30×30 μm size, is shown in fig. 6.

Since no long range correlation exists in the irregular patterns, the contributions from different parts of the surface average out so that macroscopically a stationary reaction rate results. The absence of long range synchronization indicates that gas phase coupling is no longer effective under the conditions where irregular spatial patterns are observed. One can therefore distinguish between two different oscillatory regions depending on the degree of spatial self-organization. An upper temperature window exists where gas phase coupling synchronizes the surface such that macroscopic rate oscillations can be observed, while in the lower temperature window synchronization is no longer efficient so that only local oscillations can be obtained. The transition from synchronized behavior to irregular patterns is associated with the lifting of the hex reconstruction by an increasing adsorbate coverage and with the breakdown of gas phase coupling. An overview of the development of different patterns and their relationship to the existence range for rate oscillations is given in fig. 1b.

4. Discussion and conclusions

Propagating reaction fronts and more complex forms like target patterns and spirals have been observed in a number of systems, including every oscillatory reaction studied so far on single crystal surfaces with PEEM [4,16]. Quite generally, these features represent solutions to a system of reaction–diffusion equations [17] in which they arise as a consequence of the coupling of an autocatalytic step with the diffusion of the autocatalyst. Since the $NO + NH_3$ reaction exhibits a strongly autocatalytic step as demonstrated by the occurrence of a “surface explosion”, it is no surprise to find these phenomena here as well.

The PEEM observations of the present work demonstrate the structural sensitivity of both NO and NH_3 decomposition, since no dissociation is observed on the reconstructed surface. In addition the PEEM images show the important role surface defects play in the surface reaction, since they often form the triggering center in target patterns or the core in spirals. Similar observations have been made in the $NO + CO$ reaction on Pt(100), and in both cases the particular role of surface defects can be explained with an enhanced dissociation probability for NO at these sites [18].

The most important result of the PEEM investigations was the identification of three distinct grey levels which could be associated with different surface adsorbate phases, while the transitions between them were connected with the corresponding mechanistic steps. Thus, the spatial organization on the reacting surface provides a rough picture of the mechanism of the oscillations:

Starting with an unreactive hex phase (grey area), NO adsorption first lifts the hex reconstruction, then the adsorbed NO dissociates and produces a 1 × 1-NO_{ad}/O_{ad} phase (dark area). While a 1 × 1 surface fully covered with molecular NO inhibits NH_3 adsorption, with increasing NO dissociation the inhibition will no longer be effective and NH_3 can adsorb and decompose. The atomic hydrogen reacts with atomic oxygen to form H_2O and nitrogen desorbs as N_2 until the NO_{ad}/O_{ad} layer is replaced by a NH_x adlayer (bright area). Therefore, with ongoing reaction the NO_{ad}/O_{ad} coverage finally drops below the critical value to maintain a 1 × 1 substrate structure, and the hex phase reappears. The first two of these three transitions were seen to proceed via propagating reaction fronts and therefore probably involve autocatalysis. Only the restoration of the hex phase (transition bright to grey) took place continuously without a sharp boundary.

Although the spatial structures resolved with PEEM require oscillatory conditions, one can suspect that a similar kind of spatial organization in the reaction also exists outside oscillatory conditions. One would then expect to find a kind of island mechanism with islands no longer of macroscopic dimensions but of microscopic size below the resolution of our microscope ($\approx 1\ \mu m$). This assumption can be justified since the attractive and repulsive interactions between the adparticles which cause island formation will also exist independently of oscillatory conditions. In the present case, these interactions arise mainly as a result of the $1 \times 1 \rightleftharpoons$ hex phase transition, since the higher adsorption energy on the 1 × 1 phases forces the adparticles into 1 × 1 islands [19]. However, in order to see how the length scale in island formation changes from microscopic to macroscopic dimensions requires a mathematical model which takes microscopic correlations into account, and such a model is at the present time not available [20].

In summary, the present PEEM investigation of the oscillatory $NO + NH_3$ reaction on Pt(100) demonstrated a broad spectrum of spatiotemporal patterns, ranging from homogeneous oscillations (in space and time) and regular pattern formation like spirals and target patterns to the formation of turbulent spatiotemporal patterns on the catalyst surface. In addition, the investigations demonstrate the insight that spatially resolved measurements of surface reactions can offer for clarifying the reaction mechanism of heterogeneously catalyzed gas phase reactions.

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References

[1] T.T. Tsotsis and R.A. Schmitz, Chem. Eng. Sci. 27 (1982) 1555.

[2] M.P. Cox, G. Ertl and R. Imbihl, Phys. Rev. Lett. 54 (1985) 1725.

[3] H.H. Rotermund, S. Jakubith, A. von Oertzen and G. Ertl, J. Chem. Phys. 91 (1989) 4942.

[4] S. Jakubith, H.H. Rotermund, W. Engel, A. von Oertzen and G. Ertl, Phys. Rev. Lett. 65 (1990) 3013.

[5] G. Veser and R. Imbihl, J. Chem. Phys., in press.

[6] S.J. Lombardo, F. Esch and R. Imbihl, Surf. Sci., submitted.

[7] S.J. Lombardo, M. Slinko, T. Fink, T. Löher, H.H. Madden, F. Esch, R. Imbihl and G. Ertl, Surf. Sci., in press.

[8] C.G. Takoudis and L.D. Schmidt, J. Phys. Chem. 87 (1983) 958, 964.

[9] Th. Fink, J.-P. Dath, R. Imbihl and G. Ertl, J. Chem. Phys. 95 (1991) 2109.

[10] M. Slinko, T. Fink, T. Löher, H.H. Madden, S.J. Lombardo, R. Imbihl and G. Ertl, Surf. Sci. 264 (1992) 157.

[11] M.W. Lesley and L.D. Schmidt, Surf. Sci. 155 (1985) 215.

[12] T. Fink, J.-P. Dath, M.R. Bassett, R. Imbihl and G. Ertl, Surf. Sci. 245 (1991) 96.

[13] W. Engel, M.E. Kordesch, H.H. Rotermund, S. Kubala and A. von Oertzen, Ultramicroscopy 36 (1991) 148.

[14] H.P. Bonzel, G. Brodén and G. Pirug, J. Catal. 53 (1978) 96.

[15] G.B. Fisher, Chem. Phys. Lett. 79 (1981) 452.

[16] G. Veser and R. Imbihl, in preparation.

[17] A.S. Mikhailov, *Foundations of Synergetics*, Vol. 1 (Springer, Berlin, 1991).

[18] W.F. Banholzer, Y.O. Park, K.M. Mak and R.I. Masel, Surf. Sci. 128 (1983) 176.

[19] P.A. Thiel, R.J. Behm, P.R. Norton and G. Ertl, J. Chem. Phys. 78 (1983) 7448.

[20] D.G. Vlachos, L.D. Schmidt and R. Aris, J. Chem. Phys. 93 (1990) 8306.