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By means of photoemission electron microscopy as spatially resolving method, the effect of high coverages of coadsorbed potassium ($0.16 \leq \theta_K \leq 0.21$) on the dynamical behavior of the $H_2 + O_2$ reaction over a Rh(110) surface was investigated. We observe that the originally bistable system is transformed into an excitable system as evidenced by the formation of target patterns and spiral waves. At K coverages close to saturation ($\theta_K \approx 0.21$) mass transport of potassium with pulses is seen. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4903187]

I. INTRODUCTION

Chemical waves on catalytic surfaces have been investigated intensely in the past three decades.[1–3] Mainly in single crystal studies simple reactions like catalytic CO oxidation or catalytic NO reduction were investigated on noble metal surfaces under low pressure conditions ($p < 10^{-3}$ mbar). In several studies, the effect of the addition of alkali metals to pattern forming reaction systems was explored.[4–10] Alkali metals play an important role in heterogeneous catalysis where they are used as so-called electronic promoters.[11] Well known examples are the ammonia synthesis after Haber-Bosch and the Fischer-Tropsch synthesis. Their interaction with transition metal surfaces have been in the focus of many surface physics studies.[11]

On transition metal surfaces alkali metals are highly reactive and very mobile. It is therefore not surprising that their influence on pattern forming reactions is determined by strong energetic interactions with coadsorbates. As a consequence of these interactions which include attractive as well as repulsive interactions new types of patterns may evolve. This was demonstrated with two catalytic reactions on a K-promoted Rh(110)surface, the $O_2 + H_2$ and the $NO + H_2$ reaction. The Rh(110) surface was chosen as substrate because of its enormous structural variability as evidenced by a large number of different reconstructions induced by adsorbates.[12] In the case of $O_2 + H_2$ reaction, the strong attraction between K and O caused their condensation into coadsorption islands resulting in the formation of Turing-like stationary concentration patterns. How periodic structures can develop in a system governed by attractive interactions has been explained with the concept of reactive phase separation.[6,13] In the excitable system Rh(110)/NO + H₂, the addition of potassium gave rise to the new phenomenon of pulses transporting potassium.[8–10] The analysis showed that the chemical attraction between K and O was not sufficient to explain the mass transport but that, instead, the repulsive interactions between coadsorbed

potassium and atomic nitrogen are presumably responsible for pulses transporting potassium.[8,10]

In this report, we revisit the system Rh(110)/K/O₂ + H₂ but in contrast to previous studies where the K coverage was moderate with $\Theta_K \approx 0.08$, we focused on the behavior at high K coverages with $\Theta_K > 0.16$; i.e., close to the saturation coverage of a monolayer at $\Theta_K = 0.21$.[14] At such high coverages, the originally bistable reaction is transformed into an excitable system as evidenced by the appearance of target patterns and spiral waves. Moreover, we observe a mass transport of potassium with pulses. These observations indicate that at high K coverages novel feedback mechanisms come into play causing a variety of new wave patterns even with a reaction as simple as the $O_2 + H_2$ reaction.

II. EXPERIMENTAL SETUP

The reaction was studied in a standard UHV system equipped with LEED (low-energy electron diffraction), and photoemission electron microscopy (PEEM) as spatially resolving method.[14] In PEEM experiments, UV light from a deuterium discharge lamp with maximum emission of 5.2–6.2 eV photon energy is focused onto the sample into a small spot (≈ 2 mm²). The emitted photoelectrons are collected by an electrostatic three-lens system, amplified by a channel plate, and then imaged onto a phosphorous screen. The images are recorded with a CCD camera and digitalized. PEEM images the local work function with a spatial resolution of 0.1–1 μm resolution and a temporal resolution of 20 ms. For all PEEM images shown in this work, the contrast was enhanced using image processing because we aim to study qualitatively the dynamical behavior of the reaction system.

The Rh(110) sample was prepared by cycles of repeated Ar^+ ion sputtering (E = 1 keV, $p_{Ar} = 2 \times 10^{-5}$ mbar, t = 20 min), oxidation ($p_{O2} = 3 \times 10^{-6}$ mbar), and annealing at T = 1200 K (t = 1 min). The sample was heated via direct resistive heating, and indirectly, using electron bombardment through a filament behind the backside of the crystal. Gases of purity 5.0 for hydrogen and oxygen (both Linde AG) were

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used. Potassium was deposited using a SAES getter source. In order to calibrate the K coverage, LEED patterns of the various K-induced reconstructions and their corresponding K coverages taken from the phase diagram of Rh(110)/K were used.[15] The substrate structures in the series of K-induced (1×n) reconstructions with n = 2, 3, 4 are all based on the missing-row principle; the order of appearance observed for increasingly higher θ_K is the following: $\theta_K = 0.04$: (1×4) (low coverage), $\theta_K = 0.07$: (1×3) (low coverage), $\theta_K = 0.12$: (1×2), $\theta_K = 0.16$: (1×3) (high coverage), and $\theta_K = 0.21$: (1×4) (high coverage).

III. RESULTS

In the unpromoted system, reaction fronts initiate transitions between a reactive state with an almost adsorbate free surface and an unreactive state where a high oxygen coverage inhibits hydrogen adsorption.[16,17] At moderate K coverages ($\theta_K = 0.08$), fronts can still be seen but these fronts are transporting potassium and they are transients on the way to a stationary concentration pattern as the asymptotically stable state.[4,5] In our experiments, we start with a high K coverage of $\theta_K = 0.16$ under reaction conditions with a large excess of oxygen. The surface in PEEM appears homogeneously dark reflecting an oxygen covered surface. Patterns are initiated by stepwise reducing the oxygen partial pressure until bright spots develop on the surface. As shown by Fig. 1(a), these bright spots act as nucleation centers for pulses forming target patterns or spiral wave fragments.

The dark area in the PEEM images can be unambiguously assigned to chemisorbed oxygen which is known to strongly increase the work function (≈ 1 eV at maximum).[18]
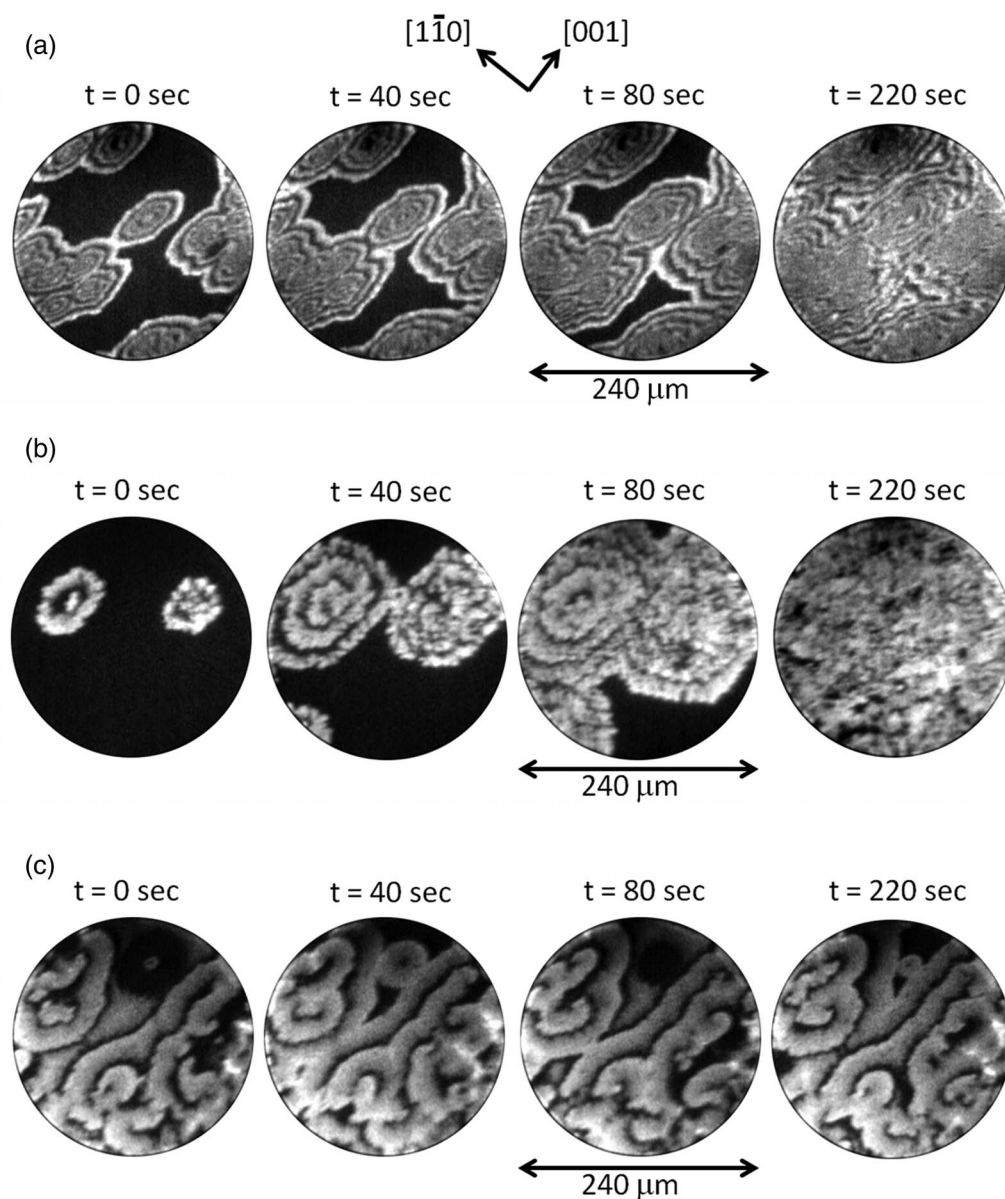
FIG. 1. PEEM images showing target patterns and spiral waves observed at medium K-coverage ($\theta_K = 0.16$) in the H$_2$+O$_2$ reaction. In each case, pattern formation was initiated by an oxygen partial pressure decrease. Experimental conditions: (a) T = 480 K, $p_{O2} = 1.1 \times 10^{-5}$ mbar, $p_{H2} = 4.5 \times 10^{-6}$ mbar, (b) T = 590 K, $p_{O2} = 1.0 \times 10^{-5}$ mbar, $p_{H2} = 4.5 \times 10^{-6}$ mbar, (c) T = 540 K, $p_{O2} = 2.0 \times 10^{-6}$ mbar, $p_{H2} = 1.0 \times 10^{-6}$ mbar.

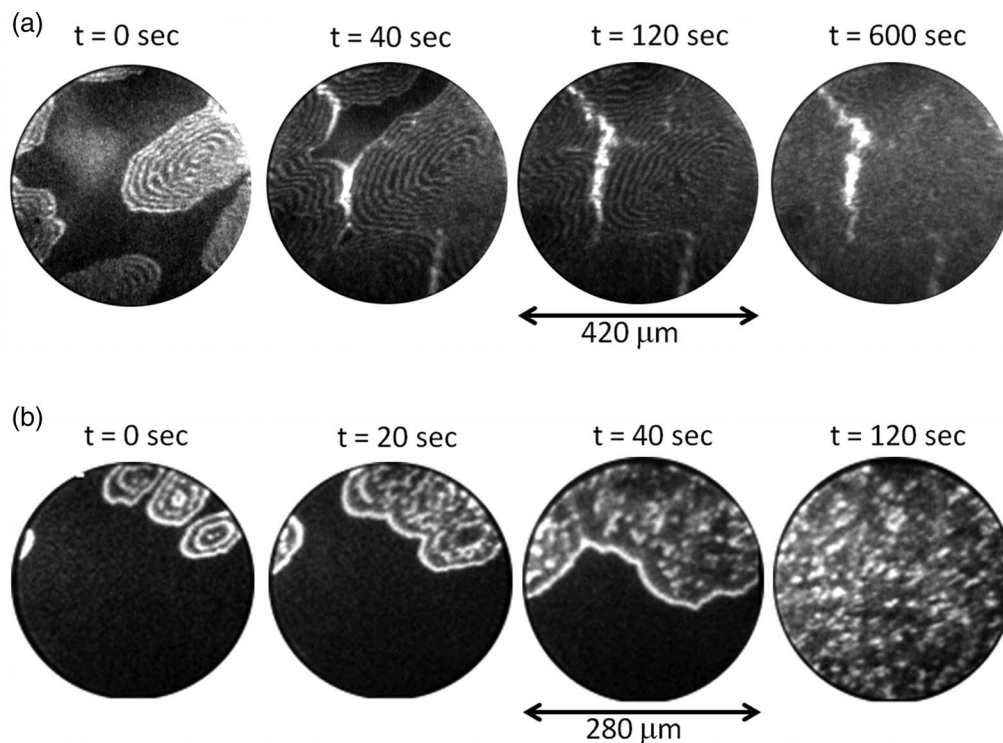FIG. 2. Target patterns and K mass transport observed at a K-coverage close to saturation of one monolayer ($\theta_K \approx 0.21$) in the H_2+O_2 reaction as recorded via PEEM. Experimental conditions: (a) T = 550 K, $p_{O2} = 4.0 \times 10^{-6}$ mbar, $p_{H2} = 5.5 \times 10^{-6}$ mbar; (b) T = 580 K, $p_{O2} = 6.0 \times 10^{-6}$ mbar, $p_{H2} = 1.0 \times 10^{-5}$ mbar.

In the K-free reaction system, the bright areas would simply represent a largely adsorbate free surface area but since potassium is known to strongly lower the work function the bright stripes representing pulses in Fig. 1 might also be associated adsorbed K or with K + O coadsorbate.[9] The original contrast in the unprocessed PEEM images at 480 K is quite weak but with rising temperature the contrast improves as demonstrated by the images in Fig. 1(b) recorded at 590 K. The target pattern in Fig. 1(a) rapidly becomes disordered as the pulses start to disintegrate into wave fragments. One notes that already the first pulses in Fig. 1(b) exhibit a ragged shape apparently indicating some kind of front instability. At both temperatures, at 480 K and at 590 K, the patterns decay within the first 3 min into a completely disordered state which is still dynamic and which probably can be best characterized as chemical turbulence. The excitable behavior of the reaction system also persists when the pressure is reduced by one order of magnitude; i.e., from 10^{-5} to 10^{-6} mbar. As shown by Fig. 1(c) the reduced total pressure has increased the pulse width from ≈ 7 μm at 1.5×10^{-5} mbar total pressure to ≈ 20 μm for 3×10^{-6} mbar. Simultaneously, the pulse velocity decreased from 0.92 μm/s at 10^{-5} mbar, 590 K, to 0.26 μm/s at 10^{-6} mbar, 540 K. For K coverage $\theta_K = 0.16$, we find excitability in a temperature range extending from 450 K to 600 K; below 450 K the contrast in PEEM becomes very weak so that the surface appears homogeneous in PEEM.

When we increase the K coverage until saturation reached at $\theta_K = 0.21$, the system is still excitable but one observes a new type of behavior as illustrated in Fig. 2(a). The pulses are more stable at this coverage and one observes the nucleation of target patterns with regular spaced pulse trains.

In the area where pulses from different target patterns collide very bright spots develop. These bright areas grow with each pulse collision. The very bright areas can clearly be attributed to potassium because their brightness is higher than that of the clean surface and potassium is known to cause on a clean surface a work function decrease of up to 4 eV below the level of the clean metal surface.[9] The fact that the bright areas grow with each subsequent pulse collision indicates that each pulse transports a certain amount of potassium so that an accumulation can take place in the collision area. Nearly exactly the same behavior of mass transport with pulses has been observed before in the NO + H$_2$ reaction on a K-promoted Rh(110) surface.[8–10] Increasing the temperature from 550 K to 580 K leads initially to the same development as at lower temperature but already after a few seconds the pulses disintegrate leading to a disordered state. This sequence is illustrated in Fig. 2(b).

IV. DISCUSSION

The examples given above demonstrate that high K coverages transform an initially bistable reaction system into an excitable system. What was not seen in the parameter range studied here but what one would perhaps expect from the attraction K–O, are stationary concentration patterns formed by large K–O coadsorbate islands. Since the diffusion of potassium is driven by oxygen we no longer have Fickian diffusion but this type of diffusion represents an example for cross-diffusion.[19] The stationary concentration patterns driven by K + O attraction develop at medium K coverages but high K coverages apparently suppress such structures.

The spatio-temporal patterns observed at relatively high potassium coverages in Fig. 2(a), look rather similar to the target patterns observed in the NO + H$_2$ reaction over both, unpromoted and K-promoted Rh(110) single crystal surfaces.[8–10,18] There are also a number of differences. In contrast to the NO + H$_2$ reaction, the present system exhibits a pronounced front instability as demonstrated by the PEEM images in Figs. 1 and 2. Formally, front instabilities can be introduced into reaction-diffusion systems by implementing a certain nonlinear dependence of the propagation velocity of chemical waves on the curvature.[20,21] This leaves the question after the physical origin of the front instability open which can only be answered by first establishing a mechanism for the excitation of pulses.

The decisive difference between the present system and the NO + H$_2$ reaction over Rh(110), however, is the following. In the NO + H$_2$ reaction, already the unpromoted system exhibited excitability and the addition of potassium was considered to leave basically the excitation mechanism of the unpromoted NO + H$_2$ reaction system intact. Here, the situation is quite different because the unpromoted system displays no excitability at all. The excitation mechanism here must therefore be directly connected to the alkali metal itself. An entirely new excitation mechanism must therefore be operating here.

The first step in the excitation mechanism is evidently a reaction front that reactively removes chemisorbed oxygen. The initial step is identical to the step forming a reaction front in the bistable system at zero or low to medium K coverages. Different from the bistable reaction system, however, the state with a low oxygen coverage is not stable but the system returns to the initial state of an oxygen covered surface. The destabilization of the low-oxygen coverage state has to be caused by the high K coverage because at low to medium K coverages this state remains stable. A possible feedback mechanism might be that after the reactive removal of oxygen K from the surrounding K+O coadsorbate diffuses back into the O-freed area.[22] The presence of K is known to decrease the H$_2$ sticking coefficient and if O$_2$ sticking would remain high, at the end oxygen adsorption would win transforming the surface into an oxygen covered area again.[17] This is a purely hypothetical excitation mechanism and detailed structural and chemical information is required for further substantiation of such a mechanism. Another tool to get more insight into the dynamics of the system could be a characterization of the turbulent regime by nonlinear time series analysis applied to digitized intensity of the PEEM images (e.g., Figs. 1(a) and 1(b), t > 300 s).[23]

A striking similarity between this system and the system Rh(110)/K/NO + H$_2$ is that the PEEM images demonstrating the transport and the accumulation of potassium (Fig. 2(a)) look almost identical.[8] This again leads to an interesting problem because it has been postulated that repulsive interactions between the potassium and chemisorbed nitrogen in the pulses are responsible for the mass transport in the NO + H$_2$ system.[8,10] These repulsive interactions of the nitrogen pulses were supposed to push K atoms across the surface similar to a broom sweeping dust. In fact, only a certain percentage of the potassium on a given spot of about 10% is transported in each pulse so that the "nitrogen broom" is quite imperfect.[8] But here no nitrogen species exists on the surface. One therefore has to conclude that either a completely different mechanism for alkali mass transport has to operate here or that the earlier mechanistic picture drawn for mass transport in the NO + H$_2$ system has to be revised.

A change in the K coverage from low to high coverage has as consequence also a qualitative modification in the character of the binding state of adsorbed potassium. At low coverage, the K atoms are adsorbed in an ionic state, while increasing K coverages lead to a growing metallic character of the adsorbed layer. This change in the binding state of adsorbed potassium is associated with a change from repulsive interactions caused by the presence of dipoles to attractive interactions prevailing in a metallic layer. Attractive interactions would certainly facilitate the accumulation of potassium as it is seen, for example, in the PEEM images of Fig. 2. Whether this change in the character of the binding state of potassium really plays a role in the accumulation of potassium needs again to be verified by further experimental studies.

V. CONCLUSIONS

In summary, we have demonstrated that the addition of a large amount of alkali promoter can transform an originally bistable system into an excitable system. The behavior of the system resembles largely that of the NO + H$_2$ reaction on Rh(110) but the excitation mechanism has to be based on a different principle. In order to obtain a mechanistic picture, evidently techniques are required that allow one to give a structural and chemical characterization of the different surface phases along a pulse profile so that it becomes clear which new phases area induced by the presence of high K coverages.

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