Ordered phases in alkali redistribution during a catalytic surface reaction

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Reaction fronts in the \( \text{O}_2 + \text{H}_2 \) reaction on a Rh(110) surface preloaded with potassium have been shown to be associated with a redistribution of the potassium from the oxygen freed to the still oxygen covered parts of the surface. As stable final state a stationary pattern results under reaction conditions formed by K + O coadsorption islands of macroscopic size. Here low energy electron microscopy (LEEM) in combination with mirror electron microscopy (MEM), photo electron emission microscopy (PEEM) and small area selected LEED (μ-LEED) were used to identify ordered phases in this process in situ and to resolve fine structures in the reduction fronts. In the \( \text{O}_2 + \text{H}_2 \) reaction without coadsorbed alkali metal a \( (2 \times 2)p \, 2 \text{mg} \) and a \( c(2 \times 6) \) were identified besides the \( c(2 \times 8) - \text{O} \) and the \( (1 \times 1) \) representing oxygen covered and oxygen freed surface, respectively. With coadsorbed potassium one finds in the front region a \( (2 \times 2)p \, 2 \text{mg} \) and further inside the oxygen covered area a dominant \( (1 \times 2) \) reconstruction with satellite spots reflecting a \( (n \times 2) \) K + O coadsorption structure with \( n = 8-12 \). In the stationary pattern a \( (8 \times 2) – \text{K} + \text{O} \) structure forms the core of the coadsorption islands while the boundary region exhibits a \( (2 \times 2)p \, 2 \text{mg} – \text{K} + \text{O} \) overlayer as ordered phase.

1. Introduction

The adsorption of alkali on transition metal surfaces has always been one of the favorite subjects of surface science studies. The initial motivation has been to improve the yield of thermally emitted electrons by adding alkali metal to a cathode. Today the main interest in this subject is focused on the role of alkali metals as electronic promoters in many important catalytic reactions. Based on spectroscopic studies and theoretical investigations a consistent picture was established in which the promoter effect was explained as being due to a local modification of the electronic surface. Spatially resolving methods demonstrated that, aside from the formation of local coadsorbate structures, also a large scale redistribution of the alkali metal takes place under reaction conditions leading to reaction fronts transporting the alkali metal and resulting in macroscopic coadsorbate islands in the μm to mm range as stable final state.

The selforganization of alkali metals in a reactive environment was demonstrated with the \( \text{O}_2 + \text{H}_2 \) reaction on a potassium promoted Rh(110) surface, using PEEM and scanning photoelectron microscopy (SPM) as spatially resolving in situ methods. In addition, metastable impact electron emission microscopy (MIEEM) was applied for imaging fronts in this system. It was shown that the initiation of reaction fronts leads to a depletion of potassium on the oxygen freed area such that at the end a stationary pattern forms consisting of macroscopic K + O coadsorbate islands surrounded by an oxygen and potassium depleted surface area. Subsequent studies showed that the main factors explaining the formation of these non-equilibrium structures were (i) the strong affinity between oxygen and potassium, (ii) a high mobility of potassium on the reduced surface and a low mobility on the oxygen covered surface, and (iii) a strong reduction of the oxygen reactivity in the presence of coadsorbed potassium. A mathematical model based on these mechanistic elements could reproduce the essential findings of the experiment.

Motivated by these findings the adsorption system Rh(110)/K and the coadsorption system Rh(110)/K + O were investigated with LEED and scanning tunneling microscopy (STM). In both systems a wide series of reconstruction phases (\( 1 \times n \) and \( 2 \times n \) with \( n = 2, 4, 6, 8 \)) was discovered whose periodicity in the [001]-direction is based on “missing rows” similar to the well known O-induced reconstructions in Rh(110)/O. The aim of this study was to show the occurrence of these ordered phases in the selforganization processes under reaction conditions with low energy electron microscopy (LEEM) and selected small area electron diffraction (μ-LEED). An identification of the ordered phases will be important for an understanding of the energetic driving force of the K + O condensation process as well as for explaining diffusion anisotropy and the reactivity towards H₂.

2. Experimental

The experiments were performed in an ultra-high vacuum LEEM instrument which has been described in ref. 11. Basics of the LEEM method have been outlined in ref. 12. For this article...
images were taken in the LEEM and in the MEM mode without using the energy filtering possibilities of this microscope. In addition, the instrument can be operated in the PEEM mode by introducing a D₂ discharge lamp as a UV photon source. In LEEM the surface is imaged by reflected and/or diffracted electrons, in MEM the incoming electrons are reflected by the sample potential before impinging onto the sample. Due to different work functions at a heterogeneously covered specimen it is possible to image simultaneously one part of the sample in the LEEM and another part in the MEM mode. This is the case, when the potential of the incoming electrons is set between the work function barrier of the oxygen covered Rh(110) (high work function) and the reduced Rh(110) surface (lower work function). In the following this mode is indicated as LEEM/MEM. The contrast mechanism in MEM and PEEM is based on differences in the local work function (WF). In the MEM mode areas with a higher WF appear bright because of the higher reflection coefficient at the WF barrier. Areas with a lower WF appear darker because less electrons are reflected due to the interaction with the sample. In PEEM a low WF is imaged as bright area, a high WF as dark area. Therefore the image contrast in MEM compared to PEEM is opposite. The majority of the LEEM images were taken in the bright field mode where the zeroth order LEED spot was used. To get a better contrast for certain superstructures fractional order LEED spots were selected by the contrast aperture for imaging. This is the dark field mode. Changing the imaging modus requires a readjustment of the whole image the orientation of the crystallographic axes changes depending on magnification and imaging mode. Therefore the crystallographic axes here can only be determined indirectly from anisotropic front propagation.

The Rh(110) specimen has already been used in previous experiments. Before and after introduction to the LEEM it was processed with several cycles of Ar ion sputtering, annealing at 1400 K and oxidation at 1000 K. As an indication for sufficient cleanliness a sequence of oxygen-induced reconstructions with increasing oxygen coverage was visible in LEED ((1 × 1)–(2 × 2)–(2 × 6)→c(2 × 8)). High purity gases (H₂: 99.9993% and O₂: 99.999%) were introduced into the LEEM object chamber by UHV leak valves. The potassium was evaporated by a K-dispenser and the cleanliness was again checked by studying the sequence of LEED patterns with increasing coverage. The K coverage was approximately \( \theta_K \approx 0.08 \) ML in the experiments. Sample heating is provided by electron bombardment from the backside of the specimen for flash and high temperature annealing. During the reaction the sample is heated by radiation from a tungsten filament. The temperature is measured by a W/Re thermocouple and the calibration of the thermocouple has been checked by an optical pyrometer. The temperature stability during an experiment is better than 2 K due to the inertia of the sample holder after it has reached an equilibrium. The absolute and difference pressures were measured by a Penning-type vacuum gauge and the ratio of the gases has been controlled by a differentially pumped mass spectrometer. All pressures given here have been corrected.

### 3. Results and discussion

#### 3.1 The O₂ + H₂ reaction

The system Rh(110)/O₂ + H₂ is bistable, i.e. reaction fronts initiate transitions between a nonreactive high oxygen coverage state and a reactive state with low adsorbate coverage, so that both gases, O₂ and H₂ can adsorb unhindered and react. Front propagation in this system has already been studied with PEEM. LEED observations in this study reported that the high oxygen coverage phase can be associated with a np(10 16)–O structure and the low coverage phase with a (1 × 1) phase. However, since the area probed with LEED (≈0.5–1 mm) was much larger than the length scale of the patterns, no fine structure of adsorbate patterns in the front region could be resolved.

The system Rh(110)/O exhibits a whole series of different O- induced reconstructions which in principle could all be present if the front profile would just represent a cross section through the (equilibrium) phase diagram Rh(110)/O. The following structures have been observed in the system Rh(110)/O₂ at \( T > 500 \) K: (1 × 3), (2 × 3), (2 × 2)–(2 × 6)–c(2 × 8). High purity gases (H₂: 99.9993% and O₂: 99.999%) were introduced into the LEEM object chamber by UHV leak valves. All pressures given here have been corrected.

#### Fig. 1

Front propagation in the O₂ + H₂ reaction on Rh(110). A reaction front was initiated at \( T = 550 \) K and \( p(O₂) = 4 \times 10^{-9} \) mbar by raising \( p(H₂) \) up to \( 2.2 \times 10^{-7} \) mbar. The front velocity was 0.1 μm s⁻¹. (a) MEM image with “Red.” and “Ox.” marking the oxygen freed and still oxygen covered part of the surface. Electron energy close to zero. (b) PEEM image recorded with a D₂ discharge lamp (5.5–6 eV photon energy) as photon source. (c) μ-LEED images taken while the front was passing an area of 1 μm diameter probed by the LEED beam. \( E = 45.0 \) eV. (d) Dark field LEEM images recorded with the (0,1/2)-beam (\( E = 41 \) eV) and the (1/2,7/8)-beam (\( E = 49 \) eV) reflecting the abundance of the (2 × 2)–p2mg and the c(2 × 8)-O structure, respectively.
demonstrate a sharp front profile with the contrast in MEM being opposite to that of PEEM. Since adsorbed oxygen on Rh(110) is known to increase the work function the bright part of the MEM image and the dark part of the PEEM image, respectively, can be identified with oxygen covered surface. Upon selecting a probe area of \( \approx 1 \mu m \) diameter with an aperture one observes the following sequence of structures as the reduction front passes the area probed by \( \mu \)-LEED: \( c(2 \times 8), \ c(2 \times 6), \ (2 \times 2)p2mg, \) and \( (1 \times 1) \). Dark field images with the \( (0 \times 1/2) \) - and the \( (1/2 \times 7/8) \) -beams displayed in Fig. 1d show that the width of the \( (2 \times 2)p2mg \) whose presence is reflected by an intense \( (0 \times 1/2)-beam \) is \( \approx 5-15 \mu m \) depending of the direction of front propagation. The sharp front profile in PEEM/MEM seems to contradict this but one has to keep in mind that in a WF vs. oxygen coverage relation the strong WF increase takes place already before completion of the \( (2 \times 2)p2mg \) structure while the subsequent coverage increase is associated with an almost plateau-like behavior of the WF. 15

3.2 The \( \text{O}_2 + \text{H}_2 \) reaction with \( K \)

Similarly to the bistable system without potassium one observes also with potassium reduction fronts but the fronts are associated with a redistribution of the potassium from the oxygen freed part of the surface to the still oxygen covered part. 4,5 In the front region a strong enrichment of potassium has been found, i.e. the fronts transport potassium. 4,5 The fronts are transients slowing down with changing K-profile until they finally stop when a stationary pattern is reached. The present work focuses on the fronts leading to a stationary pattern and on the stationary pattern itself.

Front propagation. In the following we first take a look at the structures in a propagating reduction front before studying the coadsorbate phases in the stationary patterns that finally result. Fig. 2 displays a series of \( \mu \)-LEED images taken at various positions along the front together with a K concentration profile recorded in an earlier SPEM experiment under similar conditions. The oxygen concentration profile is known from earlier SPEM measurements. 4,5 In the vicinity of the front it is basically a step-like profile from \( \theta_0 \approx 0 \) to \( \theta_0 \approx 0.7-0.8 \) with the step coinciding roughly with the steep rise of the K concentration. Due to mutual stabilization of oxygen and potassium the adsorptive capacity for oxygen can, however, increase beyond one monolayer with rising K coverage. The oxygen freed part of the surface exhibits the \((1 \times 1)\) pattern of the non-reconstructed surface. Apparently the K-coverage at this part is below \( \theta_K \approx 0.035 \) ML, the coverage above which a \((1 \times 4)\) reconstruction is induced. 6,9 The LEED result agrees with the SPEM profile shown in Fig. 2c taken under comparable conditions.

In the front region we observe in a \( \approx 10 \mu m \) wide range a \( (2 \times 2)p2mg \) but with a very intense \((0,1/2)\)-beam and a less intense \((1/2,0)\)-beam. This indicates a dominant \((1 \times 2)\) structure in this region. In the following K O adsorption region which extends over 500 \( \mu m \) the LEED pattern is dominated by an intense \((1 \times 2)\) structure. In the range with the highest K concentration we note weak satellite beams indicating an 8 to 12 fold periodicity in the \((110)\)-direction. Further inside the oxygen covered area the satellite beams move towards the integral order beams while simultaneously becoming streaky and losing intensity. Apparently structures with a higher periodicity in the \((110)\)-direction are formed. The satellite beams completely vanish at \( \approx 400 \mu m \) distance.

The phase diagrams Rh(110)/K and Rh(110)/K+O have been mapped out in detail. 9 With potassium only one observes with increasing K coverage a series of \((1 \times n)\) “missing row” reconstructions with LC denoting the structures at low and with HC at high K coverage: \((1 \times 4)\) LC, \( \theta_K = 0.035 \) ML; \((1 \times 3)\) LC, \( \theta_K = 0.075 \) ML; \((1 \times 2), \) \( \theta_K = 0.12 \) ML; \((1 \times 3)\) HC, \( \theta_K = 0.16 \) ML; \((1 \times 4)\) HC, \( \theta_K = 0.21 \) ML. At medium to high potassium coverage \((\theta_K > 0.08 \) ML\) one obtains above 470 K a variety of different surface structures with increasing oxygen exposure. Upon cooling down to 300 K the following LEED patterns are seen (at different oxygen coverages): a \((2 \times 2)p2mg\), a \((1 \times 2)\), and a continuous transition from a \((2 \times 4)\) to \((3 \times 4)\), and a series of structures of \((n \times 2)\) with \( n = 8-12 \). Depending on the preparation conditions, the \((8 \times 2)\)-structure is found in coexistence with a \((2 \times 4)\) phase.

As visible in Fig. 2, during the LEEM experiments no such coexistence were found. STM measurements demonstrated that the basis of the \((8 \times 2)\) structures is formed by the well known \((1 \times 2)\) “missing row” reconstruction of the Rh(110) surface. 9 The high periodicities of the \((n \times 2)\) structures in the \((110)\)-direction with \( n = 8-12 \) are due to rows of \((n-2)\) close-packed Rh atoms in the \((110)\)-direction separated by one missing Rh atom from the next Rh row. From the recorded ordered phases from Fig. 2 we conclude that the phases found in LEEM during reaction conditions are consistent with the phase diagram at medium to high potassium coverage. Turning off the \( \text{O}_2 \) or \( \text{H}_2 \) supply results in homogeneous distribution of potassium on the reduced and on the completely oxygen covered surface, respectively. In the first case LEED exhibits a \((1 \times 2)\) structure. In the second case, a \((1 \times n)\) reconstruction with \( n \) depending on the K coverage appears.

Dark field images of a propagating reduction front are reproduced in Fig. 3. Fig. 3b was recorded with

![Fig. 2](image-url)
Stationary patterns. Stationary patterns result when two colliding fronts slow down with shrinking distance between them until they finally stop. By varying the sliding fronts slow down with shrinking distance between them. For comparison, an image taken with the \((1\overline{2},1\overline{2})\)-beam of the \((1 \times 2)\) reconstruction. \(E = 29\) eV. A thin bright stripe indicates that this structure is restricted to an only \(3\) \(\mu\)m wide region in the front. A \((1 \times 2)\) pattern with \(n\) being around 12. A comparison with corresponding SPEM data yields a K coverage \(\frac{0.014 \pm 0.033}{0.14\) \(\mu\)m width in the center of the dark gray band is clearly discernible in this image. A \(\mu\)-LEED image reveals that the dark band is associated with a \((n \times 2)\) structure with \(n\) being around 12. A comparison with corresponding SPEM data yields a K coverage \(\theta_k \approx 0.14\) \(\pm 0.03\) \(\mu\)m. In the following a retraction of the two fronts was induced by decreasing \(p(H_2)\). This led again to a stationary pattern but now with a larger central region that expanded to 35 \(\mu\)m as demonstrated by Fig. 5c. The periodicity in the [110]-direction is now lost and the whole K + O coadsorption island displays a \((1 \times 2)\) pattern in LEED. Apparently the redistribution of potassium over a larger area has led to a lower K coverage in the condensed phase where the long range order in the [110]-direction is now absent.

**Fig. 3** Dark field imaging of a propagating reaction front in the system Rh(110)/K/O2 + H2. Experimental conditions: \(\theta_k \approx 0.08\) ML, \(T = 383\) K, \(p(O_2) = 2.0 \times 10^{-2}\) mbar, \(p(H_2) = 3.5 \times 10^{-2}\) mbar. (a) \(\mu\)-LEED images recorded at \(E = 49\) eV. (b) Dark field LEEM image with the \((1\overline{2},1\overline{2})\)-beam whose intensity mainly reflects the abundance of the \((2 \times 2)\) structure. In the reduced part of the \((2 \times 2)\) structure seen here the long range order in the [110]-direction is now absent.

**Fig. 4** Ordered phases in the large K + O coadsorption island obtained as stationary pattern in the reaction system. Experimental conditions: \(\theta_k \approx 0.08\) ML, \(T = 573\) K, \(p(O_2) = 2.0 \times 10^{-2}\) mbar, \(p(H_2) = 3.5 \times 10^{-2}\) mbar. (a) \(\mu\)-LEED images reflecting the structure at different points of the K + O island as indicated in (b). \(E = 49\) eV. (b) Schematic representation of the various structures in the K + O island using the gray level code introduced in (a). (c) K concentration profile of a K + O island determined with SPEM in a different experiment under comparable conditions. Experimental conditions: \(\theta_k \approx 0.08\) ML, \(T = 623\) K, \(p(O_2) = 1.3 \times 10^{-2}\) mbar, \(p(H_2) = 1.5 \times 10^{-2}\) mbar. (d) MEM/LEEM image (electron energy close to zero) and PEEM image of the left boundary of the K + O island. The correlation with the various LEED structure determined in (a) is indicated by the bar on top of the images.

The SPEM profile shown in Fig. 4c taken under comparable conditions is in agreement with these results. Remarkably, the MEM/LEEM and PEEM images in Fig. 4d show the opposite contrast of the corresponding images in Figs. 1a and 1b due to the K-induced lowering of the WF of the oxygen covered surface area.

If the experiment is conducted such that the two fronts approach to a distance of 22 \(\mu\)m one obtains the MEM/LEEM image displayed in Fig. 5a. A darker stripe of \(\approx 4\) \(\mu\)m width in the center of the dark gray band is clearly discernible in this image. A \(\mu\)-LEED image reveals that the dark band is associated with a \((n \times 2)\) structure with \(n\) being around 12. A comparison with corresponding SPEM data yields a K coverage \(\theta_k \approx 0.14\) \(\pm 0.03\) \(\mu\)m. In the following a retraction of the two fronts was induced by decreasing \(p(H_2)\). This led again to a stationary pattern but now with a larger central region that expanded to 35 \(\mu\)m as demonstrated by Fig. 5c. The periodicity in the [110]-direction is now lost and the whole K + O coadsorption island displays a \((1 \times 2)\) pattern in LEED. Apparently the redistribution of potassium over a larger area has led to a lower K coverage in the condensed phase where the long range order in the [110]-direction is now absent.
Various aspects of ordered alkali layers influencing diffusion on molybdenum surfaces have been addressed by Nauvome's et al. In catalytic CO oxidation on Pt and Rh field emitter tips an enhanced concentration of coadsorbed Li was observed in the reaction front region, proven by the in situ imaging of the reaction by the field desored Li+ions. A review of the surface crystallography of alkali metal adsorbed on metal surfaces can be found in. What has been demonstrated with the present system is that alkali metal on a catalytic metal surface may undergo selforganization to form large scale patterns on the surface. The LEEM measurements here add structural information. They show that redistribution of potassium occurs through well ordered coadsorbate phases of K+O. Superimposed on a dominating (1×2) structure we see that potassium induces structures with a high periodicity in the [110]-direction. At the maximum K coverage, θK ≈ 0.25 ML, we have n = 8 but with decreasing K coverage the unit cell grows in the [110]-direction reaching n = 12–14 until finally the satellite spots are no longer discernable. The aspect of anisotropy clearly present in the stationary patterns and in front propagation shall not be discussed here in further detail due to the complexity of the problem.

From local photoelectron spectra in SPEM measurements it is very likely that also an OH species is present in the coadsorbate islands, but the μ-LEED results give no indication that this species has an influence on the coadsorbate structures formed in this reaction system. Under our conditions the K coverage on the reduced surface is always so low, that the substrate either remains in a (1×1) state or that the K-inductions are just beginning to evolve. With exception of the front region where a (2×2)p2mg is present in a narrow stripe of ≈10 μm width the oxygen covered areas display the K+O coadsorbate structures which correspond to medium and high K and O coverages, i.e. the (n × 2) with n = 8–12 and a dominant (1×2) structure. The stability of the high coverage condensation phase can be attributed to (i) a kinetic stabilization by the strongly reduced reactivity of oxygen in the presence of coadsorbed potassium and (ii) to a thermodynamic stabilization as reflected by the high thermal stability of this structure. Further evidence that the (8 × 2), which appears in the condensation island in fact exhibits some particular properties was obtained in an XPS study of Rh(110)/K+O. The XPS measurements revealed that different from other coadsorbate structures the Rh 3d surface core level undergoes a significant shift of up to 0.8 eV compared to the Rh bulk component. This shift reflects a high packing density of oxygen in this structure.

4. Conclusions

It was shown that the redistribution of potassium in the O2+H2 reaction on Rh(110)/K proceeds via ordered K+O coadsorbate phases. The boundary region of both, of the propagating fronts as well as of the condensed phase in the stationary patterns consists of an approx. 10 μm wide (2×2)p2mg-K+O structure. The interior of the K+O coadsorbate phase is apparently dominated by a 1×2 reconstruction. Superimposed on this 1×2 structure potassium induces a high periodicity in the [110]-direction so that a (n×2)-K+O structure with n = 8–12 is formed. A particular role seems to be played by the (8×2)-K+O present in the core of the condensed phase and in the high K coverage region of propagating fronts. For this structure changes in the Rh 3d peaks had been observed. Altogether the present findings helped to establish a rather detailed and consistent picture of alkali redistribution under reaction conditions in the system Rh(110)/K/O2+H2.

References