Selforganization of alkali metal on a catalytic metal surface

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The spatial distribution of potassium on an Rh(110) surface during the catalytic $O_2 + H_2$ reaction is investigated employing photoelectron emission microscopy (PEEM) and scanning photoelectron microscopy (SPEM) as spatially resolving *in situ* methods. Depending on the reaction conditions, potassium condenses reversibly into macroscopic islands where it is coadsorbed with oxygen. Mass transport of potassium with the reaction fronts is observed. Differences in the mobility and in the bonding strength of potassium on the "reduced" and on the oxygen-covered surface areas are considered to be the key factors for the formation of the stationary concentration patterns.

KEY WORDS: rhodium; $H_2 + O_2$ reaction; potassium; promoter; coadsorption; selforganization; reaction fronts; scanning photoelectron microscopy.

Alkali metals play a prominent part in heterogeneous catalysis due to their role as promoters in a number of industrial chemical processes, such as ammonia synthesis *via* Haber–Bosch or synthetic fuel production *via* Fischer–Tropsch [1]. Considerable theoretical and experimental efforts went into clarifying the nature of the alkali metal bond and the mechanism of the promoter effect [2–4]. Today the modification of catalytic activity by alkali metals is generally explained as a local effect, assuming implicitly that the alkali metal is distributed homogeneously on the catalytic surface. Here we demonstrate that this assumption is not valid and that rather the spatial distribution of the alkali metal under reaction conditions is governed by selforganization processes. We observe that, depending on the reaction conditions, the alkali metal condenses reversibly into macroscopic islands of the size of micrometers to millimeters, where it is coadsorbed with oxygen. As key factors for the formation of the stationary patterns we consider differences in the mobility and in the bonding strength of the alkali metal on the "reduced" and on the oxygen-covered surface areas.

For studying the alkali distribution under reaction conditions we chose a fairly simple system, namely the $O_2 + H_2$ reaction to H_2O on an Rh(110) surface predosed with a submonolayer coverage of potassium. Predosing was achieved by evaporating a K submonolayer quantity on the surface with the help of an SAES getter source. With photoelectron emission microscopy (PEEM) which utilizes photons from a D_2 discharge lamp (5–6 eV), the spatiotemporal dynamics of a catalytic reaction can be nicely followed, but for complex systems an assignment of the gray levels in PEEM to chemical species is no longer possible. Crucially, following the redistribution of the alkali metal, there has therefore been the use of a spatially resolved *in situ* technique that allows a chemical identification of the imaged species. Scanning photoelectron microscopy (SPEM) photons from a synchrotron source are focused into a micro-spot of $\leq 0.15\,\mu$m diameter on the sample [5]. Spatially resolved chemical images are obtained *in situ* under reaction conditions by detecting photoelectrons emitted from specific atomic core levels while scanning the sample. All experiments, *i.e.*, the dosing of the gases as well as the reaction experiments under stationary conditions, were carried out in the 10^{-7} mbar range at a sample temperature of 550 K operating the SPEM chamber as a continuous flow reactor. During the catalytic reaction, the K2p and O1s electronic levels served for monitoring lateral changes in the composition of the surface adlayer.

On an Rh(110) surface, O_2 and H_2 adsorb dissociatively at $T \leq 150$ K [6,7]. Coadsorbed H and O atoms react to form the product water, which rapidly desorbs [8,9]. Reaction fronts initiate transitions between a catalytically inactive high-oxygen coverage state and an almost active oxygen-free surface area, *i.e.*, the system $Rh(110)/O_2 + H_2$ is bistable [9,10]. Such a front is displayed in figure 1(A), where the dark area represents the oxygen-covered surface and the bright area corresponds to the oxygen-free surface. When we predose the surface with potassium (submonolayer coverage), we still observe reduction fronts, but as demonstrated by figure 1(B) large bright zones form at the front interface, which extend into the still oxygen-covered part of the surface. The work function of the oxygen-covered surface has been reduced so much by potassium that the gray levels between the oxygen-covered and the reduced surface area are hardly distinguishable. The bright zones

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reflecting a strongly reduced work function are transported with the reaction front. Both the elliptical reaction front, as well as the elongated bright zones, reflect the anisotropy of the surface caused by the trough-like structure of the Rh(110) surface. It is well known that alkali on a transition metal surface causes a strong decrease of the work function and one should accordingly associate the bright zone with alkali enrichment. In a reacting environment the potassium is, however, coadsorbed with oxygen and/or OH species, and a definite assignment of the gray levels to chemical species becomes impossible. For this reason the experiments were repeated at ELETTRA using SPEM as the spatially and chemical resolving *in situ* method.

Here we start with an Rh(110) surface first covered with ~0.08 monolayers (ML) of potassium and then exposed to O_2 until saturation (0.7 ML), so that a homogeneous distribution of potassium and oxygen over the surface results [11]. Upon introducing H_2 into the gas phase we observe the formation of reduction fronts whose development at a later stage of the reaction is depicted in figure 2. As demonstrated by the O1s and

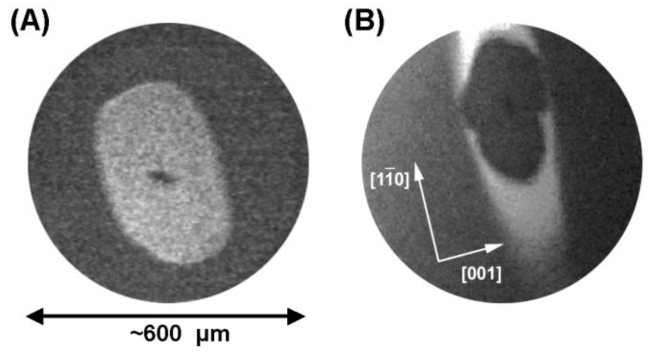

Figure 1. PEEM images showing the effect of potassium on the propagation of a reduction front in the $O_2 + H_2$ reaction on an Rh(110) surface. (A) Without potassium. A reduction front is propagating from the center outwards. Dark area represents oxygen-covered surface, bright area oxygen-free surface. Experimental conditions: $T \approx 580\,K$, $pO_2 = 2 \times 10^{-6}$ mbar, $pH_2 = 4 \times 10^{-6}$ mbar. (B) Front on a surface precovered with potassium. The area around the center from where the reduction front started exhibits a low oxygen coverage; the area surrounding the elliptically shaped front contains a high oxygen concentration. Experimental conditions: $T \approx 680\,K$, $pO_2 = 2.5 \times 10^{-6}$ mbar, $pH_2 = 5 \times 10^{-6}$ mbar. The potassium coverage is estimated to be around 0.1 ML.

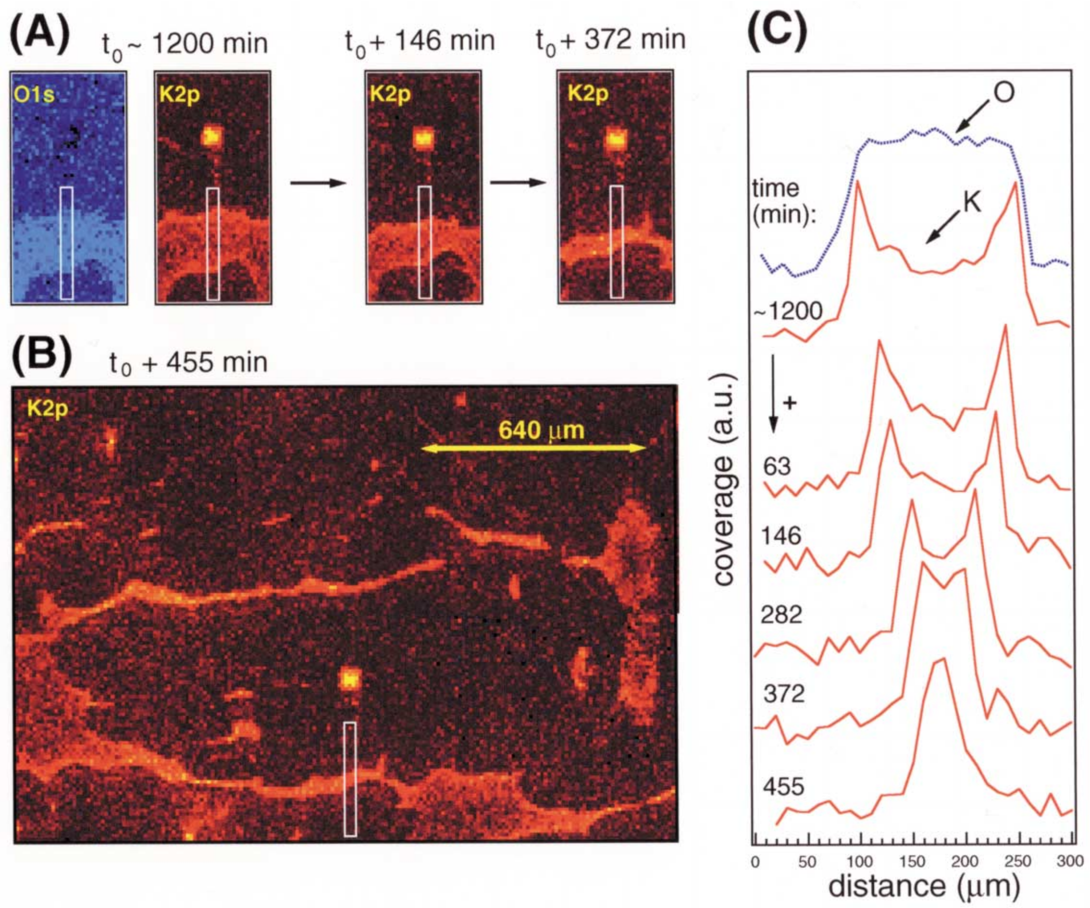

Figure 2. Potassium and oxygen distribution in the final stages of the condensation process, starting from ~1200 min after ignition of the reduction fronts. Brighter colors reflect higher count rates, *i.e.*, higher concentrations. (A) O1s image and a series of K2p images ($320 \times 640\,\mu m^2$) showing the coalescence of two reaction fronts. White rectangles mark the windows used for the intensity profiles reproduced in (C). The crystallographic [110]-direction of the Rh(110) surface is parallel to the vertical direction, as in (B). The bright feature in the K2p images is a square-shaped Pt patch acting as an easily detectable nucleation center. (B) Large scale K2p image showing a practically stationary K distribution after condensation has reached its final stage. (C) O and K coverage profiles taken along the rectangular window, indicated in (A). Experimental conditions: $T \approx 550\,K$, $pO_2 = 1.9 \times 10^{-7}$ mbar, $pH_2 = 0.8 \times 10^{-7}$ mbar.

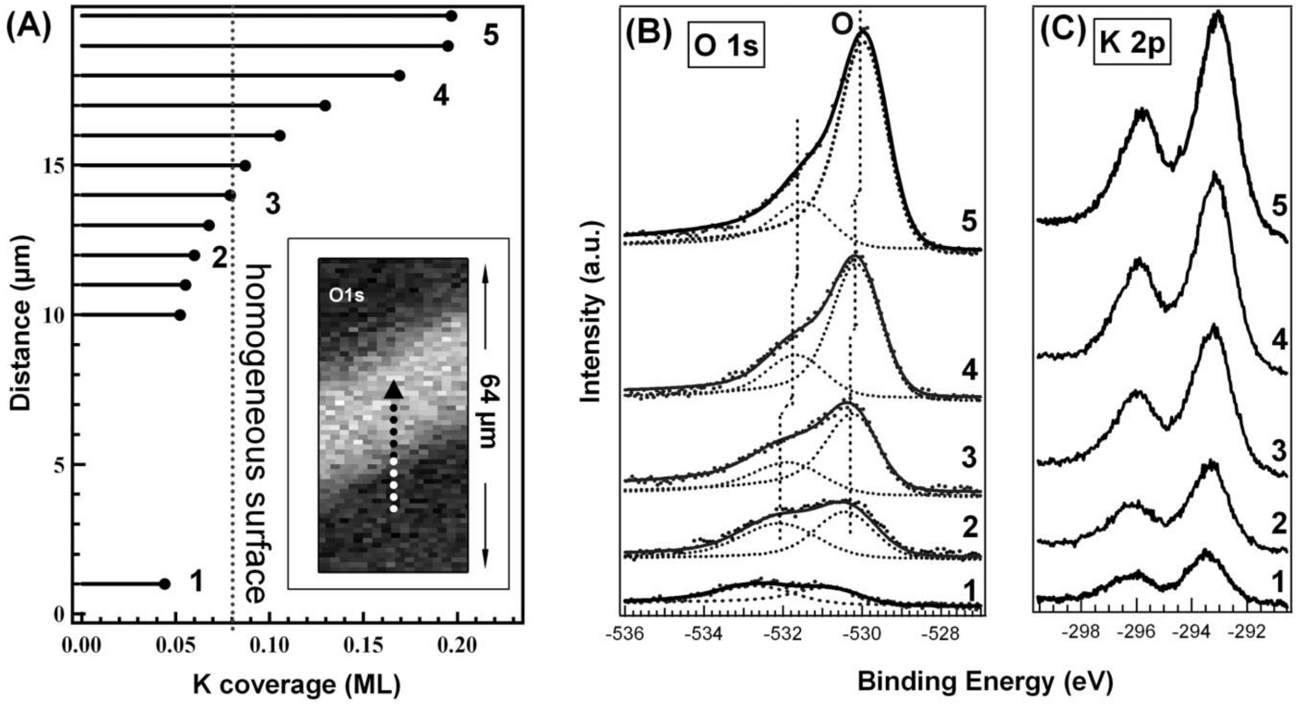

Figure 3. Chemical composition of the oxygen-covered and of the "reduced" surface demonstrated by a series of photoelectron spectra, which were taken from selected "micro-spots" after final condensation has occurred (see figure 2(B)). (A) K coverage profile across a K + O island as determined from K2p spectra, which were taken from various spots along the arrow in the inserted O1s image. The numbers 1–5 refer to various positions along this arrow, with 1 belonging to a spot on the reduced surface and 5 to a spot in the inner part of the K-O island. The coverage for the uniformly distributed potassium is denoted as "homogeneous surface". The numbers in the plot refer to the O1s and K2p spectra shown in (B) and (C). (B) O1s and (C) K2p spectra taken at the points indicated in (A).

K2p images in figure 2(A), the reduction fronts remove chemisorbed oxygen accompanied by a depletion of potassium on the "reduced" surface and a potassium enrichment on the still oxygen-covered areas. Moreover, the K coverage profiles in figure 2(C) reveal a strong enrichment of potassium in the front region. The potassium concentration inside the shrinking "oxidized" islands grows continuously with progression of the reaction fronts and finally reaches the high level of the front region ($\sim$2.2 times the initial level). In the course of the condensation process the reduction fronts slow down from initially $\sim 1\,\mu\mathrm{m/min}$ to practically zero at the end.

We can reestablish the initial situation of a uniform potassium distribution by turning off the O_2 or H_2 supply. We observe that potassium spreads out much more rapidly on a "reduced" surface, *i.e.*, when O_2 is turned off, than on the oxygen-covered surface, *i.e.*, when H_2 is turned off. Integration of the K2p signal over an area of $2.5\,\mathrm{mm}^2$ shows that mass conservation is fulfilled within our experimental accuracy of 0.01 ML, *i.e.*, what we observe is a reversible redistribution of potassium on the surface. In contrast to a simple bistable system, we cannot always reverse the direction of front motion by a parameter change. As a stable final state, we obtain a stationary concentration pattern. This pattern exists in a certain window of reaction conditions, whereas outside this window the surface homogenizes again. Since the existence of the pattern is bound to reaction conditions it is clearly a non-equilibrium structure, *i.e.*, it is part of the spatiotemporal dynamics of the system.

For identifying the surface species photoelectron spectra were taken from "micro-spots" at varying distances to the front, as indicated in figure 3(A). The two components of the O1s spectra in figure 3(B) correspond to chemisorbed O (529.9–530.3 eV) and OH (531.3–531.7 eV), the latter being stabilized by coadsorbed K [3,12]. Unfortunately, the O1s binding energies for coadsorbed CO and for carbonates are both very similar to that of the OH species, so that the origin of the corresponding component remains ambiguous [13]. In any case, the K + OH species would be present as a two-dimensional coadsorbate structure and not as a bulk component KOH, which would exhibit a different reactivity and could not be reduced at pressures as low as 10^{-7} mbar. Towards the "reduced" areas, the O1s intensity decreases, the "OH" and "O" subpeaks undergo small energy shifts and practically vanish on the "reduced" surface. We use the K2p spectra shown in figure 3(C) to monitor the K coverage. In brief, inside the "oxidized" islands a high concentration of potassium correlates with a high coverage of coadsorbed oxygen and a moderate OH (or CO) coverage.

For the condensation of potassium into a dense coadsorbate phase a thermodynamic driving force is provided by the gain in adsorption energy for potassium coadsorbed with oxygen [2–4,14,15]. The energetic stabilization can be attributed to the strong affinity between potassium and oxygen and OH, respectively. Thermal desorption experiments showed that, in fact, as well as Rh(110) coadsorbed oxygen stabilizes K on the surface, *i.e.*, depending on the K coverage, the onset of K-desorption is shifted towards higher temperature by up to 150 K, when oxygen is present on the surface [16]. A kinetic stabilization of the $K + O$ coadsorbate phase is provided by the decrease of the reactivity of oxygen towards hydrogen in the presence of potassium. This has been demonstrated in titration experiments with hydrogen [17]. Further experimental details of the system were revealed with low-energy electron microscopy (LEEM) showing that the condensation process occurs *via* a sequence of ordered $K + O$ phases on the Rh(110) surface [17]. In separate experiments, homogenous surfaces of the K/Rh(110) and $K + O$/Rh(110) system were prepared. With LEED and STM a variety of ordered K- and $K + O$-structures could be identified in accordance with the phases detected with LEEM under reaction conditions [16,18]. Simulations with a realistic mathematical model, which as an essential element contained the migration of potassium in a potential of surrounding oxygen atoms, were able to reproduce the formation of stationary concentration patterns [19].

A rather remarkable property of this system is that mass transport of potassium occurs through propagating fronts as demonstrated by figure 2(C), which leads to the pile-up of a high local K-concentration in the front region. It is conceivable that a favorable chemical environment in the front region stabilizes a high K coverage phase, but the known dependence of the potassium mobility on the state of the surface already provides a plausible explanation for the observed enrichment. As K atoms, which are very mobile on the "reduced" area, migrate to the energetically more favorable sites in the $K + O$ coadsorption phase, they will slow down as soon as they invade the oxygen-covered part. This immobilization of potassium will lead to a high potassium concentration in the front region. This mass transport of potassium with the fronts was also reproduced in the simulations so that a quite coherent mechanistic picture of the whole process exists [19].

In summary, we have shown that on catalytic surfaces with alkali metals selforganization processes can occur, destroying spatial homogeneity and resulting in a stationary concentration pattern as a final state. Real catalysts are of course in general inhomogeneous systems, but the important point here is that the heterogeneity in the promoter distribution is generated by the selforganization of the reacting system and not by the preparation of the catalyst. The resulting distribution is coupled with the spatiotemporal dynamics of the system, thus changing with varying reaction conditions. The key factors governing the redistribution of potassium are changes in the mobility and adsorption energy depending on the state of the surface. In heterogeneous catalysis, numerous alkali-promoted reaction systems exist where electron-acceptor coadsorbates (*e.g.*, O, N, OH, etc.) are present, forming stable coadsorption complexes and affecting the mobility of the alkali metal in a similar way to the example presented above. The processes observed here should therefore be important for a broad class of catalytic systems.

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