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 O2 + H2 reaction is investigated employing photoelectron emission microscopy (PEEM) and scanning photoelectron microscopy (SPM) 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; H2 + O2 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 O2 + H2 reaction to H2O on an Rh(110) surface predisposed 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 D2 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 (SPM) 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 SPM 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, O2 and H2 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)/O2 + H2 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 \( \text{O}_2 \) until saturation (0.7 ML), so that a homogeneous distribution of potassium and oxygen over the surface results [11]. Upon introducing \( \text{H}_2 \) 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 \( \text{O}_2 + \text{H}_2 \) 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: \( T \approx 580 \text{ K} \), \( p\text{O}_2 = 2 \times 10^{-6} \text{ mbar} \), \( p\text{H}_2 = 4 \times 10^{-6} \text{ mbar} \). (B) Front on a surface precoated 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: \( T \approx 680 \text{ K} \), \( p\text{O}_2 = 2.5 \times 10^{-6} \text{ mbar} \), \( p\text{H}_2 = 5 \times 10^{-6} \text{ mbar} \). 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 × 640 μm²) 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: \( T \approx 550 \text{ K} \), \( p\text{O}_2 = 1.9 \times 10^{-7} \text{ mbar} \), \( p\text{H}_2 = 0.8 \times 10^{-7} \text{ mbar} \).