Metastable impact electron emission microscopy of the catalytic H₂ oxidation on Rh(1 1 0)

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Abstract

Laterally resolved metastable impact electron spectroscopy is based on the energy analysis of electrons originating from collisions of metastable He* (2^3S) atoms with the surface, and can be used for probing the spatial distribution of surface species, i.e. for chemically resolved surface microscopy (MIEEM = metastable impact electron emission microscopy). We report upon first MIEEM results on the spectroscopic imaging of the catalytic H₂ oxidation on the clean and potassium-precovered Rh(1 1 0) surface, in which the spatio-temporal distribution of the reactants on the surface, the reaction fronts as well as the redistribution of the initially spatially homogeneous K coverage have been monitored. The results are in agreement with data previously obtained by scanning photoelectron microscopy and are discussed in terms of self-organization in the diffusion zone.
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Keywords: Metastable induced electron spectroscopy (MIES); Surface chemical reaction; Alkali metals

1. Introduction

Metastable inert gas atoms can be used as an excitation source in electron spectroscopy for metastable impact electron spectroscopy (MIES) of solid surfaces. MIES with He* (2^3S) atoms, based on energy analysis of electrons emitted in thermal collisions of long living excited He* atoms, has been developed in the last years to a powerful tool for surface analysis [1]. With suffi-

cient spatial resolution, MIES can also be used for probing the spatial distribution of adsorbates, i.e. for the laterally and chemically resolved imaging of the surface. First efforts to use this technique for the visualization of a solid surface (Au- and Cl–Al–Phthalocyanin islands on a graphite surface) were reported by Harada et al. [2] and showed the potential of metastable impact electron emission microscopy (MIEEM). In the present contribution we report upon a first attempt to apply this approach to the in situ spectroscopic imaging of a catalytic surface reaction. As a test reaction the catalytic H₂ oxidation on the Rh(1 1 0) surface was chosen, which has been imaged with a variety of microscopies: photoemission electron microscopy (PEEM, typical resolution of 0.1 μm, [3]), low

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energy electron microscopy (LEEM [4]), field electron microscopy (FEM, resolution of $\sim$20 Å, [5]) and field ion microscopy (FIM, atomic resolution, [5]). With the exception of LEEM the contrast mechanisms in these microscopies are mainly based on different work functions of the adsorbate-covered reactive surfaces: the oxidized surface appears dark (high work function) and the H_2-reduced bright (low work function) in PEEM and FEM, while it is vice versa in FIM. However, in the presence of additives, alkali atoms in particular, this simple interpretation is not applicable since alkali coadsorption drastically changes the work function already at very low coverages, possibly causing a reversed contrast. Thus, for the interpretation of in situ microscopy more sophisticated techniques, like scanning photoelectron microscopy (SPEM) have to be used. SPEM has recently rendered possible the first-time observation of self-organization effects in the surface diffusion of a potassium coadsorbate in the catalytic $H_2 + O_2$ reaction on the Rh(1 1 0) surface [6]. However, being a synchrotron-based technique SPEM is very expensive and not widely available. Thus, a synchrotron-independent, chemically resolving microscopy such as MIEEM, is very appealing. Additionally, due to the nature of the electron excitation process in MIEEM molecular orientations at surfaces can in principle be detected.

2. Experimental

In order to realize a spectroscopic MIEEM for the imaging of dynamic surface processes, an intensive He* source is needed with electron emission from adsorbate valence states, which is sufficient for fast image acquisition. The He* source used in the present work is an improved version of the one developed in Clausthal [7] and is described in detail in Ref. [8]. The He* flux density has additionally been enhanced by a magnetic hexapole which focuses the He* beam onto the sample [9]. Such a He* source combined with the spectroscopic low energy electron microscope (SpecLEEM), allows to achieve a spectral resolution of less than 1 eV and a spatial resolution of

$\sim$200 nm at 10–20 s image acquisition time. This MIEEM apparatus has also been applied recently to study the segregation of titanium and strontium oxides on $SrTiO_3$ [10].

Although the energy and lateral resolution of the apparatus is not as good as the ultimate energy and lateral resolution of the SpecLEEM in the energy-filtered mode (400 meV and 25 nm [11]), its spatial resolution is comparable to those of SPEM (90 nm are reported [6]) and allows to trace spatiotemporal processes within a field of view of about 50 μm in diameter.

MIES spectra have been achieved by integrating the intensity of a certain region of interest (about 2×2 μm in size) in a series of images of different electron energies. The variation parameter is the so-called START-voltage (STV), which corresponds to the kinetic energy of the electrons at the sample for the given microscope setting and sample work function.

3. Results and discussion

Fig. 1a exhibits the spatial hydrogen and oxygen distribution and the reaction front during the ongoing $H_2 + O_2$ reaction on the Rh(1 1 0) surface as imaged in MIEEM with electrons emitted via excitation by He* (2^3S) atoms. For comparison, the corresponding PEEM pattern is also shown. The MIES spectra in Fig. 1b demonstrate that the differences in the electron emission rate from hydrogen-reduced and oxygen-covered areas should provide a sufficient contrast between the reduced and oxidized surface, as is in fact seen in the corresponding MIEEM image.

Fig. 2 displays the spatial hydrogen and oxygen distribution and the reaction front during the ongoing $H_2 + O_2$ reaction on the K-precovered Rh(1 1 0) surface. The differences in the emission curves (Fig. 2a) for the reduced and oxidized K-precovered surface allows for sufficient contrast at different energies, whereas a contrast reversal is observed when changing from the lower energy edge to the higher kinetic energies (compare Fig. 2b and c taken at STV = 14 V and 3 V, correspondingly).
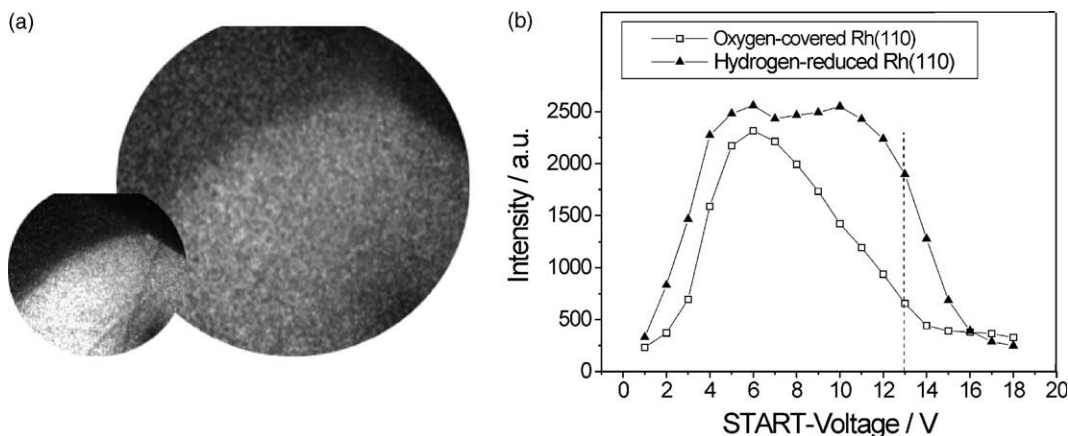
Fig. 1. (a) MIEEM visualization of the H_2 oxidation reaction on Rh(1 1 0) ($T = 560$ K, $p_{O_2} = 2 \times 10^{-7}$ mbar, $p_{H_2} = 1 \times 10^{-7}$ mbar, STV 13 V, field of view 75 μm). Dark and bright regions correspond to the oxidized and the reduced Rh surface, respectively. The inset in the left lower corner shows the reaction visualized in the PEEM-mode of our set-up. (b) Electron emission spectra for the oxygen-covered and hydrogen-reduced Rh(1 1 0) surface obtained by He* (2^3S) excitation. The difference in the electron emission rate at a particular STV of 13 V (along the dashed line) provides the MIEEM contrast in the image (a).
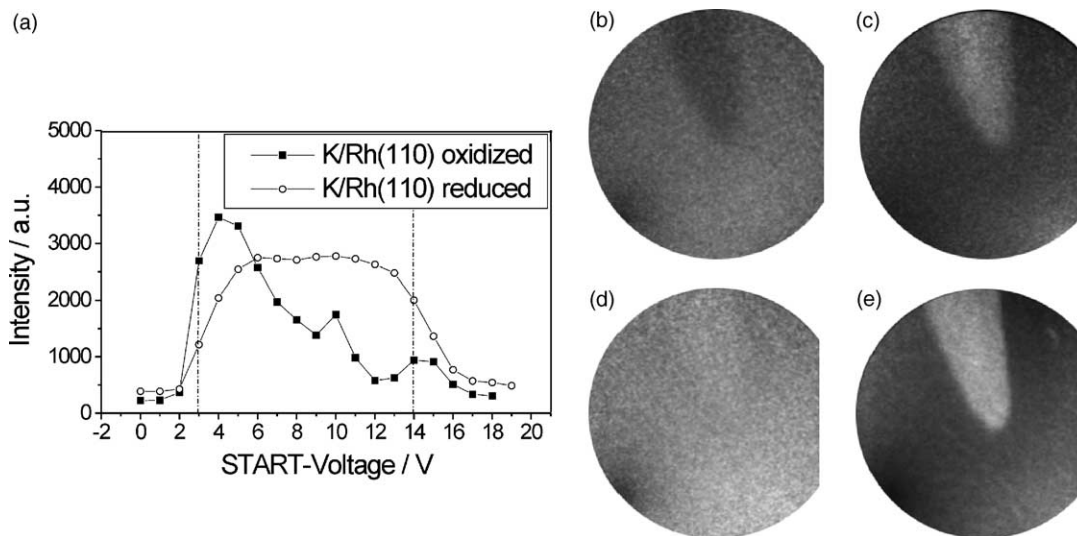

Fig. 2. Visualization of the H_2 oxidation reaction on the K-precovered ($\Theta_K = 0.17$) Rh(1 1 0) surface. (a) Electron emission spectra from the oxidized and hydrogen-reduced Rh(1 1 0) surface obtained by He* (2^3S) excitation. The peaks at STV $= 10$ V and 14.5 V for the oxidized surface are oxygen 2p and K 4s induced respectively. The differences in the electron emission rate at STV $= 14$ V and 3 V provide the MIEEM contrast in the images b and c, respectively. (b) MIEEM-image at $T = 570$ K, $p_{O_2} = 2 \times 10^{-7}$ mbar, $p_{H_2} = 1.2 \times 10^{-7}$ mbar and STV $= 14$ eV. Field of view: 50 μm. Dark and bright regions correspond to the oxidized and reduced surface, respectively. (c) Same as in (b), but at STV $= 3$ V. Note the reverse of the contrast. (d) Same as in (b), but at STV $= 6$ V, the emission curves do not provide any contrast at this voltage, see Fig. 2a. (e) Same as in (b) but imaged in the PEEM-mode of our set-up.

We were also able to reproduce the main result of the SPEM study [6], namely the redistribution of the potassium layer via surface diffusion of potassium in the presence of two different spatially

separated surface phases (oxygen covered and re-duced Rh surface). A corresponding set of video-images is presented in Fig. 3a–c. Already the PEEM image (Fig. 3a), where the dark region appears in the middle of the oxygen-covered area, points to a possible redistribution of the K-layer during the reaction, namely to a potassium en-richment in the front region. The corresponding MIEEM image taken at STV = 4 V verifies this appearance. The dark spot in the PEEM image appears, however, as a bright spot in MIEEM covering the same part of the oxidized surface, as follows from the analysis of the image-brightness profiles across the oxidized area (see Fig. 3d). In turn, the MIEEM image taken at STV = 15 V

(Fig. 3c) does not show any peculiarities within the oxidized area of the surface. The explanation of the "invisibility" of the K-redistribution in MIEEM at higher STVs is provided by the MIEEM emission spectra taken at different po-tassium coverages (Fig. 3e): one sees clearly that the coverage-related differences in the spectra are much more pronounced at lower STVs and are hardly present at higher energies. Thus, it is clear why the contrast variations caused by the K-redistribution are not present in Fig. 3c (obtained at STV = 15 V).

An explanation of the K-redistribution itself during the ongoing hydrogen oxidation on Rh(1 1 0) was given in the SPEM study [6]: the
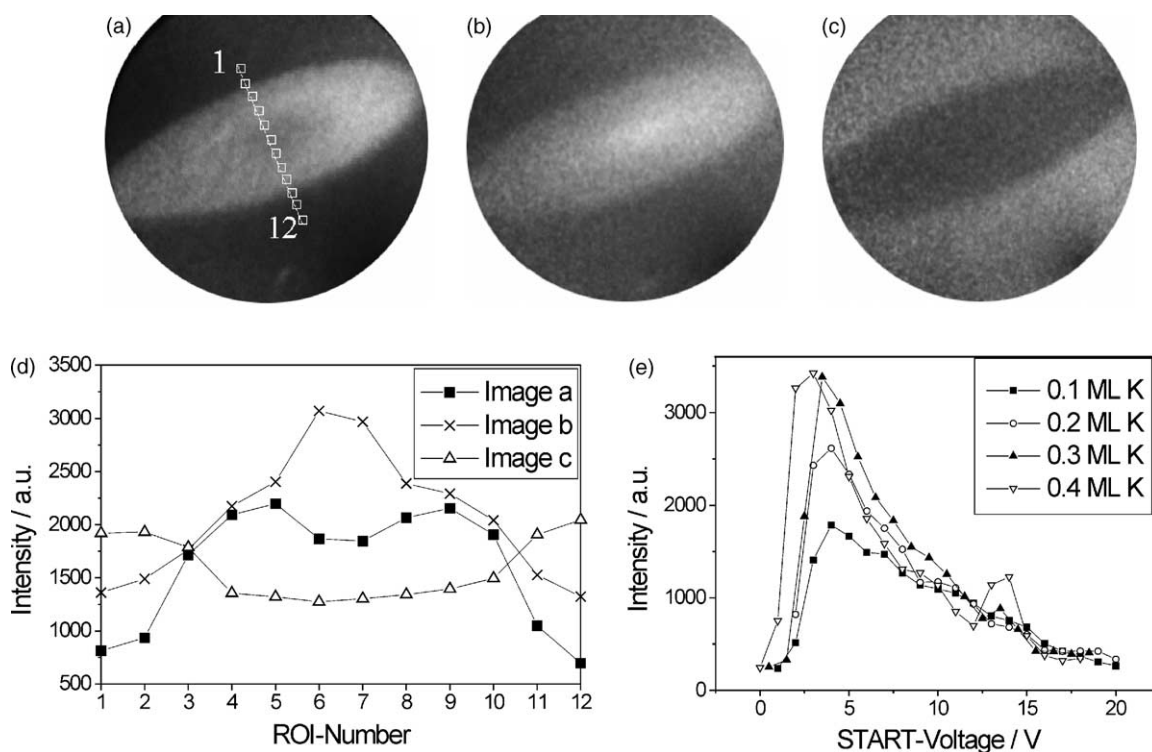

Fig. 3. Spatial redistribution of the coadsorbed potassium in the H_2 oxidation on the K-precovered ($\Theta_K = 0.2$) Rh(1 1 0) surface. (a) PEEM-image of the ongoing reaction at $T = 570$ K, $p_{O_2} = 2 \times 10^{-7}$ mbar, $p_{H_2} = 1.2 \times 10^{-7}$ mbar. The dark region in the middle of the oxygen-covered surface points to the depletion of the K-layer. (b) Same as in (a), but in the MIEEM mode (STV = 4 V). The cor-responding K-depleted region exhibits a higher electron emission. (c) Same as in (b), but at STV = 15 V; the K-depleted region is not visible. (d) Intensity profiles of the PEEM (a) and MIEEM (b, c) images as evaluated along the line of regions of interest shown in (a). (e) Electron emission spectra from the oxygen-covered and hydrogen-reduced K-precovered Rh(1 1 0) surface obtained by He* (2^3S) excitation at different potassium coverages. The differences in the emission at lower STVs are sufficient to register the changes in the K-coverage during the reaction as is seen in (b).

energetically more favorable adsorption sites of K in the oxygen coadsorbate phase lead to K diffusion due to the chemical potential gradient. Similar concentration patterns of electropositive adsorbates have been observed as a result of the up-hill diffusion in two-dimensional first order phase transitions under reaction-free conditions [12]. Similarly as in the SPEM experiments, we observed the slowing down of the propagation of the reaction fronts, an effect obviously related to the increased concentration of alkali in the front region. Recent experiments with alkali (Li) and rare earth (Dy) coadsorbates in the CO oxidation on Pt surfaces have shown a steep decrease in the reaction rate at increasing coverage of the electropositive coadsorbates [13,14]. At reaction rates close to zero one can also expect a slowing down of the propagation of reaction fronts, considering the low mobility of the dissociatively adsorbed oxygen on the alkali-precovered surface.

4. Conclusions

We have demonstrated that the electrons originating from collisions of metastable He* (2^3S) atoms with the surface can be utilized for chemically resolved MIEEM of dynamic surface processes such as surface reactions.

In situ MIEEM of the catalytic H_2 oxidation on the clean and potassium-precovered Rh(1 1 0) surface can be used to monitor the spatio-temporal distribution of the reactants and of the reaction fronts propagation as well as a laterally resolved identification of an alkali coadsorbate (K). The results are in qualitative agreement with data previously obtained by scanning photoelectron microscopy.

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