

## Spectroscopically resolved *in situ* imaging of the catalytic H<sub>2</sub> oxidation on Rh(110) by metastable impact electron emission microscopy

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Metastable rare gas atoms can be used as an excitation source in electron spectroscopy thus allowing the *Metastable Impact Spectroscopy* (MIES) of solid surfaces. MIES with He\* (<sup>2</sup>S) 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 a sufficient spatial resolution, MIES can in principle be used for the probing of the spatial distribution of adsorbates, i.e. for the chemically resolving surface microscopy. 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 show the principal possibility to realize the *Metastable Impact Electron Emission Microscopy* (MIEEM).

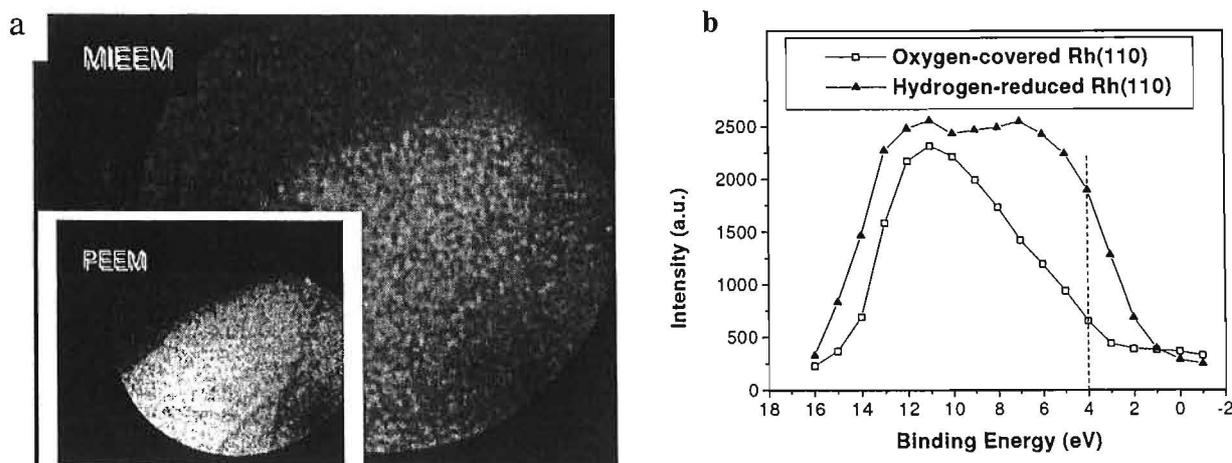
We report here our first attempt to apply this approach to the *in situ* spectroscopic imaging of a catalytic surface reaction. To realize the idea of spectroscopic MIEEM for the imaging of dynamic surface processes an intensive He\* source is needed which allows sufficient electron emission from the valence states of adsorbate for fast (within seconds per frame) image acquisition. The He\* source, recently developed in Clausthal [3] and combined with the Spectroscopic Low Energy Electron Microscope (SpecLEEM) allows to achieve spectral resolution of 1 eV and 200 nm spatial resolution at 10-20 sec image acquisition time. Although this is less than the ultimate energy- and lateral resolution of the SpecLEEM in the energy-filtered mode (400 meV and 25 nm, correspondingly [4]), it allows to trace spatio-temporal processes within the field of view of ca. 75  $\mu\text{m}$  diameter.

As a test reaction the catalytic H<sub>2</sub> oxidation on the Rh(110) surface was chosen, a reaction which has been routinely visualized with a variety of spatially resolving techniques which cover different length scales from the  $\mu\text{m}$ -region to atomic resolution. The most often used imaging methods have been photoemission electron microscopy (PEEM, [5]) which allows for a typical resolution of 0.1  $\mu\text{m}$ , field electron microscopy (FEM, [6]) with a resolution of  $\sim 20$   $\text{\AA}$ , and field ion microscopy (FIM, [6]) which gives atomic resolution. The contrast mechanisms in these microscopies are based mainly on the different work functions of reacting adsorbates: the oxidized surface appears dark (high work function) and the H<sub>2</sub>-reduced bright (low work function) in PEEM and FEM, and *vice versa* in FIM. However, in the case of studies of the effect of additives, e.g. alkali, on the reaction, this usual interpretation fails since alkali coadsorbates drastically change the work function already at very low coverages causing under obstacles a reversed contrast, i.e. the oxidized surface can appear “brighter” than the reduced one. For the identification of the surface species and thus for the interpretation of the *in situ* recorded microscopic images, more sophisticated techniques like the *Scanning Photoelectron Microscopy* (SPEM) have to be used. This microscopy has rendered possible the recent first-time observation of self-organization effects in the surface diffusion of a potassium coadsorbate in the catalytic H<sub>2</sub> + O<sub>2</sub> reaction on a Rh(110) surface [7]. However, it has to be noted that synchrotron-based techniques like SPEM are extremely expensive. Thus the use of alternative, synchrotron-independent possibilities for chemically resolving microscopy (e.g. MIEEM) is extremely

appealing for this kind of research. Additionally, due to the nature of the electron excitation process in MIEEM molecular orientations at surfaces can in principle be detected.

Figure 1a exhibits the spatial hydrogen- and oxygen-distribution and the reaction front during the ongoing  $\text{H}_2 + \text{O}_2$  reaction on the Rh(110) surface as imaged in MIEEM with electrons emitted via excitation by  $\text{He}^* (2^3\text{S})$  atoms. For comparison the corresponding PEEM pattern is shown too. The MIEEM 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.

We were also able to image the reaction in presence of a potassium submonolayer and to reproduce the main result of the SPEM study [7], namely the self-organization of the potassium layer via surface diffusion of potassium in the presence of two different spatially separated coadsorbates (hydrogen and oxygen). Here the differing binding energies of potassium in the  $\text{K}+\text{O}_{\text{ads}}/\text{Rh}(110)$  and the  $\text{K}+\text{H}_{\text{ads}}/\text{Rh}(110)$  systems lead due to the chemical potential gradient to the diffusion of K against its own concentration gradient. This results in the formation of stationary concentration patterns, similarly as observed earlier for the diffusion of Li on the Mo(112) surface under reaction-free conditions (transport of Li between the different two-dimensional phases against the Li concentration gradient [8]).



**Figure 1.** (a) MIEEM visualization of the  $\text{H}_2$  oxidation reaction on Rh(110) ( $T=560$  K,  $p_{\text{O}_2}=2 \times 10^{-7}$  mbar,  $p_{\text{H}_2}=1 \times 10^{-7}$  mbar,  $E_B=4$  eV, field of view  $75 \mu\text{m}$ ). 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(110) surface obtained by  $\text{He}^* (2^3\text{S})$  excitation. The difference in the electron emission rate at a particular binding energy of 4 eV (along the dashed line) provides the MIEEM contrast in the image (a).

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