Oxidation and Reactivity of Ru-based Model Catalysts: Synchrotron Radiation Studies

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Introduction

The processes on realistic catalysts are far too complex to allow the identification of the microscopic reaction steps. This problem calls for idealization of the experimental conditions such as the use of single crystalline surfaces and the investigations under well-controlled vacuum conditions (UHV conditions). The prize to pay for this so-called surface science approach is the introduction of a pressure and material gap by which catalytic properties (elementary reaction steps, reaction intermediates etc.) determined under well defined conditions may not be transferable to realistic reaction conditions. A prominent example for the manifestation of an apparent pressure gap was previously reported for the CO oxidation reaction over the ruthenium surface **[1]**. While under UHV conditions the Ru surface is by far the poorest catalysts among the late transitions metals, this ranking in catalytic activity reverses when the CO oxidation reaction proceeds under high pressure and oxidizing conditions. Here Ru turns out to be much more active than the other late transition metal surface. We will demonstrate that this activity transition is closely related to the formation of an ultrathin RuO_2(110) film on top of Ru(0001) surface.

Methods

In the following we will briefly explain the techniques we used to study the RuO_2(110) model catalyst. High resolution core level shifts (HRCLS) measurements of $Ru3d_{5/2}$ respectively O1s were performed in Lund (MAX II, beamline ID 311). The assignment of core level shifts to specific species on the surface is based on density functional theory (DFT) calculated core level shifts. With surface x-ray diffraction (SXRD) we studied in-situ the evolution and the decomposition of the RuO_2(110) films as a function of temperature and the partial pressures of oxidizing and reducing gases (O_2, H_2, CO). The oxidation of Ru particles in comparison with the oxidation of 100nm thick Ru films was studied by scanning photo electron microscopy (SPEM Trieste, Elettra).

Results and Discussion

The RuO_2(110) surface is produced by excessive exposure (typical $2x10^6$ L O_2, 1L = 1 Langmuir = 1.33 x 10^{-6} mbar·s) of a well-prepared Ru(0001) surface to molecular oxygen, at a sample temperature of 650K. The Ru(0001) surface oxidizes in an autocatalytic way **[2]**. Autocatalytic oxidation means that the Ru(0001) surface produces its own 'catalyst' in the form of small RuO_2 nuclei to accelerate the oxidation process.

In the bulk structure of RuO_2 the Ru atoms bind to six oxygen atoms, forming a slightly distorted RuO_6 octahedron, while the O atoms are coordinated to three Ru atoms in a planar configuration that is consistent with an sp^2 hybridization of O. The dimensions of the RuO_2(110) surface unit cell are 3.12Å x 6.38Å **[3]**. On the stoichiometric RuO_2(110) surface (cf. the ball and stick model of the bulk-truncated RuO_2 (110) surface: **Fig. 1**) two kinds of under coordinated surface atoms are present which are organized in rows along the [001] direction: (i) the bridging oxygen atoms O_{br}, which are coordinated only to two Ru atoms underneath (instead of three) and (ii) the so-called 1f-cus-Ru atoms (1f-*cus* stands for one-fold **c**oordinatively **u**nsaturated **s**ites) **[4]**. Both undercoordinated surface atoms (1f-cus Ru and O_{br}) can clearly be resolved in the core level spectroscopy **[5]** and seen in STM **[6]**.

Oxygen exposure to the stoichiometric RuO_2(110) surface leads to the population of the atomic oxygen adsorbed on-top of the 1f-cus Ru atoms (referred to on-top O) **[1]**. Exposure of CO at low temperatures (say 200K) results also in the occupation of the 1f-cus Ru atoms by upright sitting CO molecules **[1]**. As soon as the sample temperature approaches room temperature, the CO molecules recombines with adjacent bridging O atoms from the RuO_2(110) surface to form CO_2, thereby reducing the RuO_2(110) surface **[1]**.

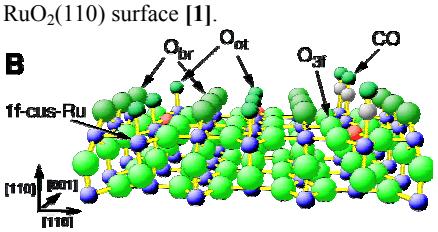


Figure 1: *Ball and Stick model of the RuO_2(110) surface on which CO and additional oxygen (O_{ot}) is adsorbed on-top of the 1f-cus-Ru atoms. The bridge bonded oxygen (O_{br}) and the under coordinated Ru (1f-cus-Ru) are indicated. Both surface species are under coordinated with respect to bulk-coordination.*

With HRCLS one can identify the undercoordinated surface atoms on RuO_2(110). This allows us to follow surface reactions on the RuO_2(110) surface, for instance the interaction of RuO_2(110) with H_2 **[7]**. (cf. **Fig. 2**)

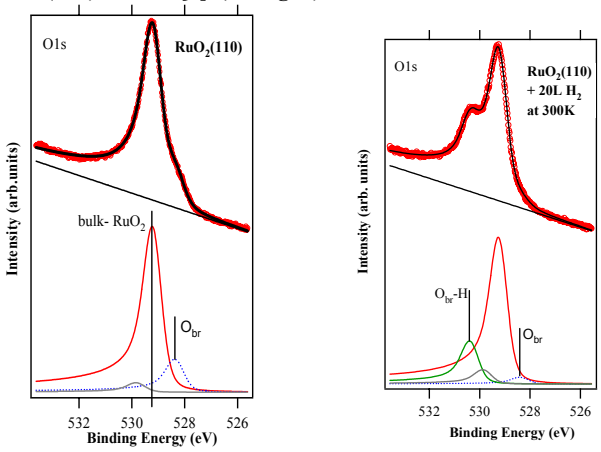


Figure 2: *O(1s)- surface core level shift spectra of the pristine RuO_2(110) surface (a) in comparison with the RuO_2 surface which was exposed to 20L H_2 at 300K. Clearly an additional signal shows up at 530.6eV; the bulk O1s peak of RuO_2 appears at 529.4eV.*

The SXRD experiment **[3]** was designed to study in-situ the oxidation of Ru(0001) in a pure molecular oxygen atmosphere. With SXRD we measured **H** scan at L = 0.2 as well as the **L** scan at (H, K) = (0.733, 0), while the Ru(0001) surface was exposed to 10^{-5} mbar of molecular oxygen, keeping the sample temperature at 630 K and 580 K, respectively (see **Fig. 3**). After an induction period of about 20 minutes a distinct diffraction peak occurs at 0.733 in the **H** scan (cf. **Fig. 3a**) which corresponds to the second order diffraction of RuO_2(110). After the induction period the x-ray diffraction intensities at H=0.733 increase steeply with exposure time, finally saturating after 60 minutes. The found induction period together with the steep raise in intensity (see inset of **Fig. 3a**) is reconciled with an autocatalytic oxidation process of Ru(0001) **[2]**. The evolution of the **H** scan does not indicate any variation in the full-width at half maximum (FWHM=0.018). Therefore the averaged lateral dimension of the RuO_2 domains along the [-110] direction is approximately 150 Å which is in line with recent STM images of RuO_2(110) films on Ru(0001) **[6]**.

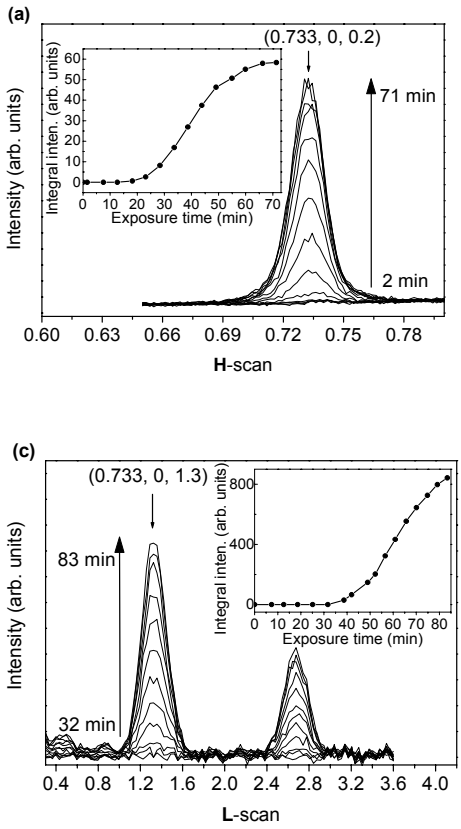
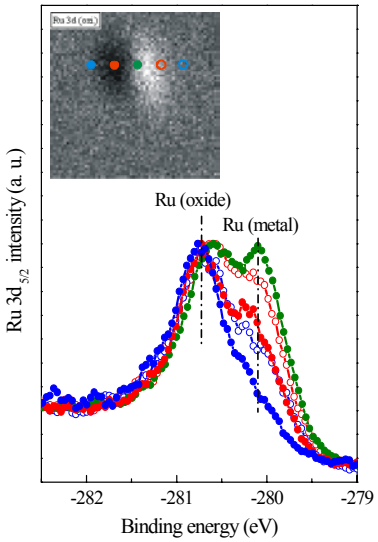


Figure 3: *Monitor the oxidation of the Ru(0001) sample by in-situ SXRD. (a) Evolution of the **H** scan with exposure time when exposing the Ru(0001) sample to $p(O_2) = 10^{-5}$ mbar at a sample temperature of 630K: In the inset the integral intensity is shown as a function of oxygen exposure time. The peak at 0.733 is the second order reflection of RuO_2(110) along the **H** direction.(c) Evolution of **L** scans with exposure time when exposing the Ru(0001) sample to $p(O_2) = 10^{-5}$ mbar at a sample temperature of 580K: In the inset the integral intensity is displayed as a function of oxygen exposure time.*

We also measured the evolution of the **L** scans for (H, K) = (0.733, 0) during the oxidation of Ru(0001) (cf. **Fig. 3c**). **L** scans probe the out-of-plane periodicity of the RuO_2(110) film. The (H, K) = (0.733, 0) diffraction beam is predominantly sensitive to the Ru sub-lattice of the RuO_2(110) film. After an induction period of about 30 minutes (cf. **Fig. 3c**) two distinct maxima evolve in the **L** scan, namely at L=1.3 and at L=2.6. From the FWHM of the peaks in the **L**-scan we estimate the thickness of the RuO_2(110) to be 1.6 nm, i.e. the RuO_2 film consists of five RuO_2 layers. Since the FWHM of the maxima in the **L** scans does not change during the oxidation of Ru(0001), the vertical growth of the RuO_2(110) oxide film is self-limited. From the separation of the maxima in the **L**-scan we infer that the Ru sub-planes in RuO_2(110) domain are separated by 3.2 Å, in perfect agreement with the bulk layer spacing of RuO_2(110) structure (3.23 Å).

With Scanning Photo Electron Microscopy (SPEM) **[8]** we studied the oxidation of a 100nm Ru film grown on MgO(100) on which also some small Ru droplets were deposited due to the Pulse-laser deposition process (PLD). From the variation of $Ru3d_{5/2}$ spectra on the position on the Ru droplet, we conclude that the Ru film is easier to oxidize than the Ru droplet. Very likely this is due to the lesser grain boundaries in the Ru droplet in comparison with the 100nm thick Ru film.



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