

High energy surface x-ray diffraction for in situ surface structure determination

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The quest for fundamental understanding of solid surfaces and their interaction with the surroundings has been a major research field for decades, motivated by important areas such as catalysis, corrosion, nanostructures and thin film electronic devices. For this purpose, a large number of experimental techniques with high surface sensitivity have been developed. Many of these techniques are used under ultra-high vacuum conditions due to limited mean-free path of the probing/detected electron or ion, and others can be used at atmospheric conditions or in liquids. Among these surface sensitive techniques insensitive to the surroundings of the sample, Surface X-Ray Diffraction (SXRD) have contributed to a novel understanding of the role of the surface in gas-surface interactions [1,2] such as catalytic reactions or electrochemical induced surface segregation in electrodes [3]. Our study [4] demonstrates the potential for in situ surface studies using high energy x-rays. It has the potential to significantly increase the fundamental structural understanding of material processes/phenomena as they happen in a real environment. The in situ structural understanding is a key parameter for development of a number of material processes of significance importance to industry and society such as catalysis, nanostructure growth and electrochemistry.

Within the proposal I-20120064-EC *Defects in catalysis – a structural study*, experiments were carried out at the beamline P07 of Petra III at Deutsches Elektronen-Synchrotron (DESY), which is designed for materials studies with hard x-ray radiation. The energy of the beam can be tuned between 30 and 200 keV and the beam itself can be focused to a spot of a few micrometers in diameter. To create the desired environment for catalytic reactions a specially designed UHV chamber/reactor was used. It allows pressures in the 10^{-10} mbar range for surface preparation as well as a controlled gas pressure up to 1 bar in the catalysis reactor chamber. The gas supply system allows to independently setting the reactor pressure, the gas composition and the total gas flow and to detect the resulting gas composition with a mass spectrometer. In Fig. 1a) we show an image of the reactor cell and the large area Perking-Elmer detector. The incident angle was tuned to close to the critical angle of Pd(100); at 85 keV the incident angle was set to 0.04° . The distance from the sample to the detector was 1.75 meters. The Pd(100) single crystal was cleaned by Ar⁺ sputtering using an ion energy of 1.5 keV in an Ar pressure of 1×10^{-5} mbar.

The procedure to collect the diffracted intensities is shown in Fig. 1. The present set-up using a large area detector combined with 85 keV photons enables a simple rotation of the sample to be sufficient for data collection. In the present case, the projection of the HK-plane of the sample under the present conditions is illustrated in Fig. 1a, in which also the angular range which the sample is rotated is indicated. As the sample is rotated, the CTRs and the superlattice rods will cross the Ewald sphere, which will give rise to the detected diffracted intensities. This is illustrated in Fig. 1b. Because of the high energy, the Ewald sphere will flatten significantly as compared to lower energies, reducing corrections of the intensities to negligible quantities and reduce the uncertainties in the data significantly.

In Figs. 1c-e images recorded during the rotational scan. As can be seen from these figures, the diffracted intensities can easily be detected, both from the CTRs and from the superlattice rods. The exposure time was 0.5 seconds. In theory, for an endless surface the detected intensity should be

point-like as the rod crosses the Ewald sphere, however because of the mosaics of the Pd(100) surface and the existence of rotational and mirror domains in the $\sqrt{5}\times\sqrt{5}R27^\circ$ on the Pd(100), the intersection appears elongated.

The total 900 images collected during the rotation can be used to form an image of the most intense pixels from each image, resulting in the image in Fig. 1f. Unprecedented, this is a comprehensive 3D data set of the surface diffraction from an oxygen induced surface oxide under highly reactive steady-state condition. It allows for an almost intermediate recognition of ordered structures on the surface. In fact, close inspection of the image easily reveals the mismatch in one direction between the distances in the ideal $\sqrt{5}\times\sqrt{5}R27^\circ$ cell and the double distance of the short side in the PdO(101) cell, which is 6.15 and 6.06 Å respectively. Thus the resolution is significantly higher than in normal Low Energy Electron Diffraction (LEED) in which this mismatch cannot be detected. Finally, it has to be pointed out that no other experimental technique sensitive to ordered surface structures of less than an atomic layer can be used under the sample environments used here.

In summary we have demonstrated the strength of HESXRD for surface structure determination during harsh catalytic conditions. It is clear that the surface structural changes into various structures as the reaction conditions change. Our measurements also demonstrate the ability to determine a surface structure during such conditions in a timescale reasonable for synchrotron measurements. The measurements also show how the structure can be followed with unprecedented time resolution and still containing structural information orders of magnitude that could previously be obtained. The experiments presented clearly indicate the potential for a number of different related surface dependent materials science phenomena such as layer-by-layer growth, electrochemistry and nanostructure formation.

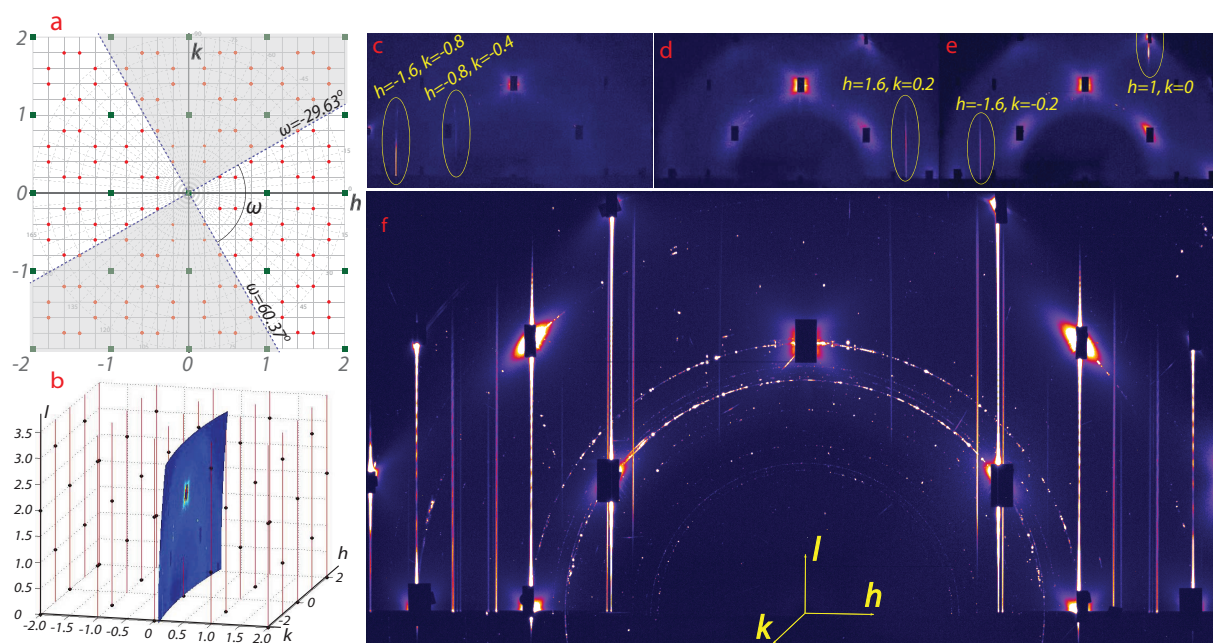


Figure 1: a) In-plane view (hk -plane projection) of the angular range measured. The CTRs from the substrate (squares) and from the $\sqrt{5}\times\sqrt{5}R27^\circ$ superlattice (dots) are shown. b) Figure illustrating how the CTRs and the $\sqrt{5}\times\sqrt{5}R27^\circ$ cross the Ewald sphere during sample rotation. c-e) Sample images from the rotational scan. f) All images collected during the rotational scan added into a single image.

References

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