

PHYSICAL REVIEW B 76, 155410 (2007)

**Oxidation of Pd(553): From ultrahigh vacuum to atmospheric pressure**

R. Westerström, J. Gustafson, A. Resta, A. Mikkelsen, J. N. Andersen, and E. Lundgren  
*Department of Synchrotron Radiation Research, Lund University, Box 118, S 221 00 Lund, Sweden*

N. Seriani and F. Mittendorfer  
*Institut für Materialphysik, Universität Wien, A-1090 Wien, Austria*

M. Schmid, J. Klikovits, and P. Varga  
*Institut für Allgemeine Physik, Technische Universität Wien, A-1040 Wien, Austria*

M. D. Ackermann and J. W. M. Frenken  
*Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands*

N. Kasper and A. Stierle  
*Max-Planck Institut für Metallforschung, Heisenbergstrasse 3, D-70569 Stuttgart, Germany*  
(Received 11 May 2007; published 11 October 2007)

The oxidation of a vicinal Pd(553) surface has been studied from ultrahigh vacuum (UHV) to atmospheric oxygen pressures at elevated sample temperatures. The investigation combines traditional electron based UHV techniques such as high resolution core level spectroscopy, low-energy electron diffraction, scanning tunneling microscopy with *in situ* surface x-ray diffraction, and *ab initio* simulations. In this way, we show that the O atoms preferentially adsorb at the step edges at oxygen pressures below  $10^{-6}$  mbar and that the (553) surface is preserved. In the pressure range between  $10^{-6}$  and 1 mbar and at a sample temperature of 300–400 °C, a surface oxide forms and rearranges the (553) surface facets and forming (332) facets. Most of the surface oxide can be described as a PdO(101) plane, similar to what has been found previously on other Pd surfaces. However, in the present case, the surface oxide is reconstructed along the step edges, and the stability of this structure is discussed. In addition, the  $(\sqrt{6} \times \sqrt{6})$  Pd<sub>5</sub>O<sub>4</sub> surface oxide can be observed on (111) terraces larger than those of the (332) terraces. Increasing the O pressure above 1 mbar results in the disappearance of the (332) facets and the formation of PdO bulk oxide.

DOI: [10.1103/PhysRevB.76.155410](https://doi.org/10.1103/PhysRevB.76.155410)

PACS number(s): 68.35.Bs, 68.37.Ef, 68.47.Gh, 68.43.Bc

#### **IV: SXR study of Pd single crystal surfaces as model CO oxidation catalysts**

*CO oxidation catalysts are nowadays widely used in industrial and automotive applications. In the near future they will also play a very important role in fuel cell technology, which is very sensitive to CO contamination. Through the use of in-situ Surface X-Ray Diffraction (SXR) we were able to unravel the atomic structure of the catalyst surface during CO oxidation, under realistic pressure and temperature conditions for different Pd single crystal surfaces. From our results we find that for all Pd surfaces the most efficient reaction path is the so-called Mars-Van Krevelen mechanism which involves the oxidation of only the outermost atomic layers of the catalyst surface. This effect is in clear contradiction with what has commonly been assumed in the field of catalysis for many years, namely that oxide formation poisons the catalyst. Combining our results on surface roughness during the oxidation of CO with results obtained with High Pressure STM [10], we can confirm several aspects of a new model for so-called self-sustained oscillations proposed by Hendriksen et al [70].*

#### **V Atomic Steps as a Motor for Reaction Oscillations**

*Atomic steps on catalyst surfaces are often considered as special, active sites for heterogeneous catalytic reactions [85]. Due to the reduced coordination, the metallic atoms at step sites can offer enhanced binding to reactant molecules [3,86,87] and exhibit enhanced activity for bond breaking [88-91]. Here we show that steps on surfaces may also play a role by changing the stability of the catalytically active phase. Our high-pressure Surface X-Ray Diffraction (SXR) experiment on a palladium model catalyst shows that a high density of steps strongly alters the conditions required for the formation of the thin palladium oxide film that serves as the active phase for the catalytic oxidation of carbon monoxide. With high-pressure Scanning Tunneling Microscopy (HP-STM) we further observe how, under steady-state conditions, reaction-induced variations in the step density lead to the periodic removal and (re)formation of this active surface oxide. We show that this new mechanism is at the heart of the well-known reaction rate oscillations during the catalytic oxidation of carbon monoxide at atmospheric pressure [75,92].*