week ending 16 DECEMBER 2005

PRL 95, 255505 (2005)

Structure and Reactivity of Surface Oxides on Pt(110) during Catalytic CO Oxidation

M. D. Ackermann, ^{1,2} T. M. Pedersen, ³ B. L. M. Hendriksen, ² O. Robach, ⁴ S. C. Bobaru, ² I. Popa, ¹ C. Quiros, ⁵ H. Kim, ¹ B. Hammer, ³ S. Ferrer, ⁶ and J. W. M. Frenken ²

¹ESRF, 6, rue Jules Horowitz, F-38043 Grenoble cedex, France ²Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands ³Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

⁴CEA-Grenoble DRFMC/SI3M/PCM17, rue des Martyrs, 38054 Grenoble cedex 9, France ⁵Departamento de Física, Faculdad de Ciencias, Universidad de Oviedo, Avda. Calvo Sotelo, s/n, 33007 Oviedo, Spain ⁶CELLS - ALBA, Edifici Ciències Nord. Mòdul C-3 centra, Campus Universitari de Bellaterra, Universita Autònoma de Barcelona, 08193 Bellaterra, Spain (Received 1 July 2005; published 16 December 2005)

We present the first structure determination by surface x-ray diffraction during the restructuring of a model catalyst under reaction conditions, i.e., at high pressure and high temperature, and correlate the restructuring with a change in catalytic activity. We have analyzed the Pt(110) surface during CO oxidation at pressures up to 0.5 bar and temperatures up to 625 K. Depending on the O_2/CO pressure ratio, we find three well-defined structures: namely, (i) the bulk-terminated Pt(110) surface, (ii) a thin, commensurate oxide, and (iii) a thin, incommensurate oxide. The commensurate oxide only appears under reaction conditions, i.e., when both O₂ and CO are present and at sufficiently high temperatures. Density functional theory calculations indicate that the commensurate oxide is stabilized by carbonate ions (CO_3^{2-}) . Both oxides have a substantially higher catalytic activity than the bulk-terminated Pt surface.

DOI: 10.1103/PhysRevLett.95.255505 PACS numbers: 61.10.Eq, 82.65.+r

III: Interaction between Pt(111), O₂ and CO at elevated pressure and temperature

In this chapter we present a series of SXRD experiments performed at high pressure and temperature on the Pt(111) single crystal surface. We have studied the interaction of CO and O₂ with this surface, as they form a classic model system for studying the catalytic oxidation of CO. We have studied the interaction of each single gas with the surface in the full range from UHV to atmospheric pressure. A very important result is the in-situ measurement of the oxidation of the Pt(111) surface, under formation of only several monoatomic layers of a-PtO₂. Secondly we have exposed the surface to mixtures of both gasses at elevated temperatures. We have measured the structure of the surface and its reactivity in the catalytic oxidation of CO simultaneously under semi realistic reaction conditions. The main result of this experiment is that we unambiguously show that the a-PtO₂ layer exhibits a much higher reactivity in CO oxidation than the bulk terminated Pt(111) surface.