Submitted to Surface Science

LBL-1707
Preprint c.1

STUDY OF SO_2 ADSORPTION ON A STEPPED PLATINUM SINGLE CRYSTAL SURFACE BY PHOTOELECTRON SPECTROSCOPY

W. Siekhaus and T. Novakov

March 1973

Prepared for the U.S. Atomic Energy Commission under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-1707
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Study of SO_2 Adsorption on a Stepped Platinum Single Crystal Surface by Photoelectron Spectroscopy*

W. Siekhaus and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, Ca. 94720

Abstract: SO_2 was adsorbed at room temperature, under UHV conditions, on a stepped single crystal surface of Pt, and observations were made with x-ray photoelectron spectroscopy (XPS-ESCA). From the observed energies and intensities of O, S and Pt photoelectron lines it is concluded that the SO_2 decomposes at the Pt surface to form a surface sulfide. Only a small fraction of that oxygen stays on the surface, probably in the molecular form.

As a part of a program of studying the surface interactions of sulfur dioxide with different materials, we have performed a study of the adsorption of SO_2 on a clean platinum single crystal surface, under UHV conditions, using the technique of x-ray photoelectron spectroscopy (XPS-ESCA).

Very little is known about the chemical species produced on metal surfaces by SO_2 adsorption in general, and on Pt in particular. The interaction of SO_2 with a clean silver surface was studied by Lassiter[1] using Auger spectroscopy, who concluded that sulfur becomes chemisorbed to the silver, probably in the form of a sulfide. No oxygen peak was detected in his Auger spectrum following the SO_2 adsorption.

The XPS measurements described in this paper were performed with an AEI ES 200 photoelectron spectrometer. Aluminum $K\alpha_{1,2}$ radiation was used to excite the photoelectrons.

*This work has been supported by the National Science Foundation-RANN and the U.S. Atomic Energy Commission

The single crystal was cut such that a 6(111) x 100 stepped surface was formed; it was electropolished and its surface structure was observed by LEED. The crystal was mounted on a platinum strip and cleaned in the spectrometer by heating at 800° - 900°C in an oxygen atmosphere of ~1 x 10^{-6} Torr for about 45 minutes. No surface impurity was observable after this treatment. The spectrometer pressure during observation was less than 1 x 10^{-9} Torr. To deposit a layer of SO_2, the crystal was exposed to ~3 x 10^{-6} Torr-sec of SO_2.

The binding energy calibration was such that graphite in electrical contact with the spectrometer and hydrocarbon (such as ethylene) on platinum both give a C(1s) binding energy of 285.0 eV. In this way the sulfur binding energies of the surface species produced by SO_2 adsorption can be compared directly with reported XPS measurements of different sulfur compounds.

The sulfur 2p, oxygen 1s, and platinum $4f_{5/2}$ - $4f_{7/2}$ photoelectron spectra of the platinum surface exposed to SO_2 are reproduced in Figure 1. A single sulfur 2p peak having a FWHM of about 2 eV is seen, corresponding to one well defined chemical state of sulfur. The S(2p) binding energy is found to be 163.5 eV. Since the value of the S(2p) binding energy for elemental sulfur is 164.2 eV, the surface sulfur shows a chemical shift of -0.7 eV relative to neutral sulfur. The chemical shift is, in the first approximation, proportional to the net charge on the atom (ion) and therefore the surface bonding must involve electron transfer from platinum to sulfur. In a separate experiment we have measured the S(2p) binding energy of PtS and found it to be 163.7 eV. This value is in close agreement with the S(2p) binding of the sulfur species produced by SO_2 chemisorption on Pt surface. We conclude therefore that the product of SO_2 adsorption on platinum is a surface sulfide resembling PtS.

As can be seen from Figure 1 the concentration of oxygen on exposed platinum is small. This oxygen is associated either with platinum oxides or adsorbed molecular oxygen produced in the process of SO_2 interaction with the platinum surface. The O(1s) binding energy is 532.9eV, which is about 2 eV higher than the binding energies of typical metal oxides. We therefore conclude that the oxygen produced on Pt surface by SO_2 adsorption probably is adsorbed O_2.

From the relative intensities of S(2_p) and O(1s) photoelectron peaks we estimate that on the Pt surface there are about four sulfur atoms per oxygen atom. This may indicate that in about 75% of the SO_2 adsorption events, leading to sulfide formation, oxygen is not retained at the surface.

Our findings for the Pt + SO_2 system seem to be in accord with Lassiter's results for the Ag + SO_2 case. Lassiter suggests a mechanism whereby the SO_2 molecule is adsorbed and subsequently broken up in such a way that sulfur becomes chemisorbed as sulfide, while the oxygen either diffuses into the bulk or evaporates from the surface.

In summary, our XPS results shown that the product of SO_2 adsorption on a stepped platinum single-crystal surface is a surface sulfide. The sulfur becomes chemisorbed on the surface via electron transfer from platinum to sulfur. The O_2 fragment of the SO_2 molecules leaves the surface in about 75% of the SO_2 adsorption events leading to the sulfide formation.

ACKNOWLEDGMENTS

We thank Professor G. A. Somorjai for providing us with the Pt single crystal. We also thank Dr. J. M. Hollander for useful comments.

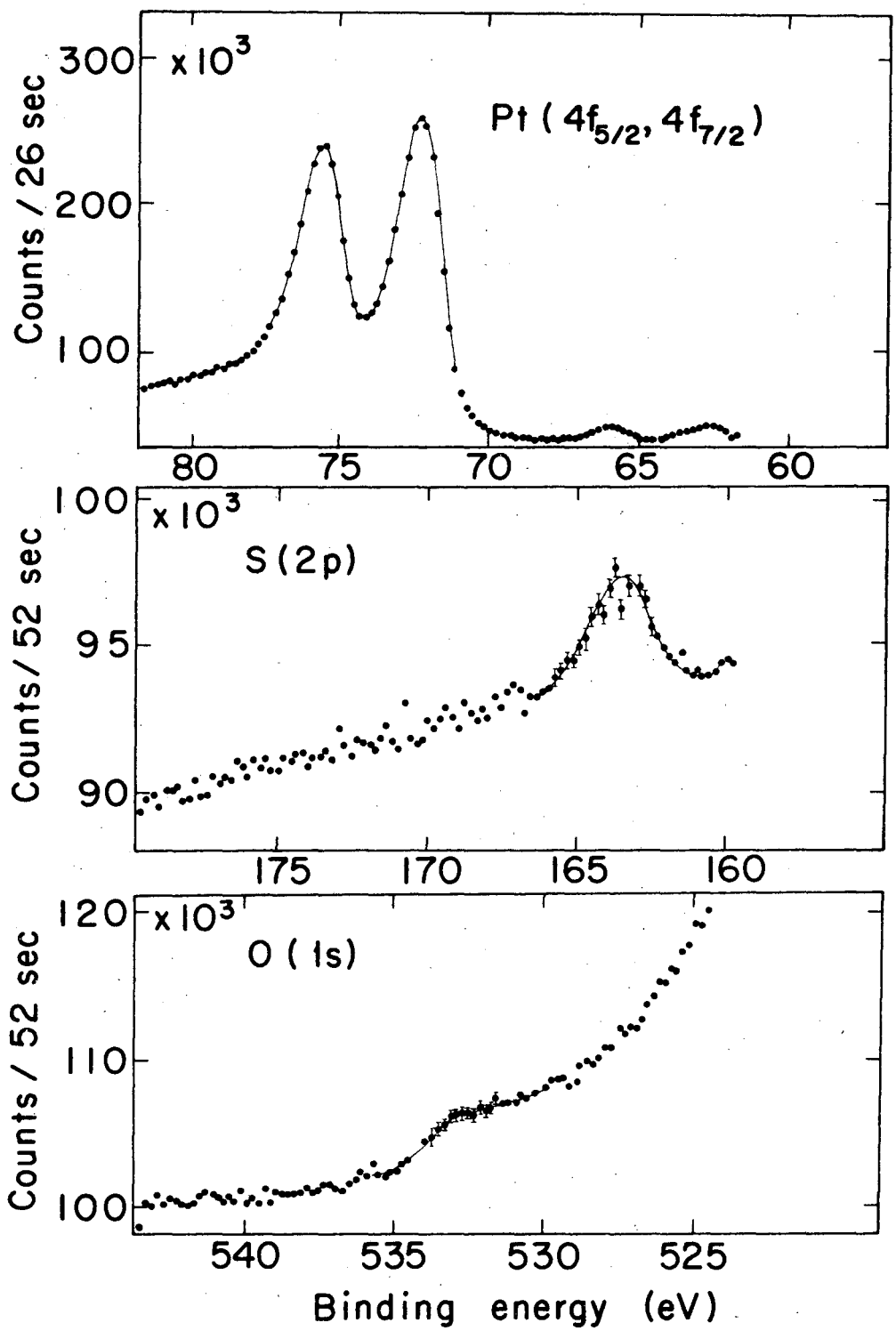
REFERENCE

1) W. S. Lassiter, J. Phys. Chem., 76, 1289 (1972).

FIGURE CAPTION

Figure 1.

Pt (4f), S(2p) and O(1s) photoelectron spectra of a stepped platinum crystal surface exposed to SO_2



XBL732-2356

Fig. 1

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720