~~C00-4341-5~~

DOE/ER/04341-5

MASTER

PROGRESS REPORT
COVERING THE PERIOD
DECEMBER 1, 1979 to NOVEMBER 30, 1980

FOR

DEPARTMENT OF ENERGY CONTRACT

DE-AC02-77ER04341.A003

Steven L. Bernasek

Steven L. Bernasek
Principal Investigator
Department of Chemistry
Princeton University
Princeton, New Jersey 08544

There is no objection from the patent
point of view to the publication or
dissemination of the document(s)
listed in this letter.

BROOKHAVEN PATENT GROUP

3/24 1981 By *CRC*

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MGW

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This progress report covers the period December 1, 1979 to November 30, 1980 of a study of the mechanism of chemical poisoning of model heterogeneously catalyzed reactions on well characterized transition metal surfaces. This study is supported by the Department of Energy under contract DE-AC02-77ER04341.A003. The objectives of our research during the period covered by this progress report are first outlined. Progress in each of these areas during the past year is then described. Information about the personnel involved in this work during the past year, and a bibliography of articles prepared for publication is included at the end of this report. Copies of publications prepared during the past year describing work supported by this contract are also included.

The objectives of our work during the past year can be divided into two areas. Specific objectives in these areas and progress toward achieving these objectives will be described in turn. The two objective areas are surface structural characterization and poisoning reaction dynamics. Specific objectives in the general area of surface structural characterization during the past year were the characterization of the clean Mo(001) surface, the characterization of the adsorbed overlayer resulting from exposure of the Mo(001) surface to COS, and the characterization of the clean Co(0001) surface. Progress toward each of these objectives has been good.

The structural characterization of the clean Mo(001) surface using the constant momentum transfer averaging method of Lagally (1) has been completed. Our analysis, based on a LEED data base of nine diffraction features over 44 angles of incidence, suggests a first layer contraction of 10% of the bulk interlayer spacing. This is in agreement with the work of Clarke (2) and Ignatiev, et. al. (3). This work is described in two manuscripts presently in press (4).

As a result of this work, we have established contacts with two experts in the field of multiple-scattering LEED structural analysis, Dr. H-D Shih, and Dr. M. A. Van Hove. They have supplied state of the art multiple-scattering programs (5) to our group for future use in LEED analysis. We hope to use these programs in addition to the single-scattering methods used in the clean Mo(001) work. We hope that the availability of the multiple scattering approach will improve the accuracy of model structures obtained by single-scattering data averaging structural searches.

Another outgrowth of our structural work on the clean Mo(001) surface is an interest in the design and choice of R-factor formalisms (6) for quantitative LEED analysis. We are applying techniques of sensitivity analysis (7), developed for the study of gas phase scattering problems, to the analysis of proposed R-factor formalisms. We hope that this sensitivity analysis approach will be useful in the rational choice of R-factors appropriate for LEED structural analysis.

We have completed the LEED data collection for the diffraction resulting from exposure of the clean Mo(001) surface to COS. This pattern is a $c(2 \times 2)$ pattern, and we have collected data over fifteen angles of incidence for about twenty separate diffraction features. Our work with the clean Mo(001) surface has indicated that this data base should be sufficient for structural analysis of this overlayer, as a wide variation in azimuthal angle has been included in this work (8). We are presently analyzing and averaging this photographically recorded data base.

Surface characterization of the clean Co(0001) surface during the past year has been devoted to developing reproducible and reliable methods for cleaning the Co(0001) surface in UHV. This is especially difficult due to cobalt's reactivity, and its low temperature structural transition which severely limits annealing temperatures. Intensity data collection is presently underway for this surface.

Specific objectives in the general area of poisoning reaction dynamics during the past year were related to clean and sulfur exposed molybdenum and cobalt catalyzed small molecule decomposition reactions. Studies of the decomposition of HCOOH on the clean Mo(001) surface were extended to lower surface temperatures with the addition of a liquid nitrogen cooled sample holder to the system. The decomposition appears to be complex even at adsorption temperatures as low as we can obtain with the present holder. Also, the recent addition of a higher sensitivity Auger detector indicates that some of our earlier results may have been affected by the presence of a very small amount of oxygen on the molybdenum surface. Work is continuing in this area.

Thermal decomposition dynamics studies of HCOOH decomposition on the COS and thiophene exposed Mo(001) surface area are also continuing. This aspect of our studies has been hampered somewhat by problems with the software controlling our Auger spectrometer, and a shortage of personnel in the first part of the year. These problems have now been solved for the most part, and the work in this area is proceeding.

Personnel

During the period covered by this progress report, two graduate students, one postdoctoral associate, one undergraduate and the principal investigator have been involved in this work. The principal investigator presented seminars on the work described in this progress report to the national meeting of the American Institute of Metallurgical Engineers, the Princeton University Department of Chemistry, American Cyanamid's heterogeneous catalysis group and the French-American Conference on Heterogeneous Catalysis and Related Areas of Surface Chemical Physics. Dr. Charles Schramm has worked primarily on the studies of the Co(0001) surface during the past year and was supported by DOE funds throughout the year. Mr. Jerry Olszewski, who did most of the LEED structural work described

in this report has completed his graduate work and is presently writing his thesis. He presented a paper on the structural analysis of the Mo(001) surface at the IBM conference on the Determination of Surface Structure by LEED in June. Mr. Olszewski was supported by a University honorific fellowship during the academic year, and by DOE funds during the summer. Ms. Susan Miles worked primarily on the clean and poisoned surface decomposition dynamics studies during the past year. She was supported by DOE funds throughout the year, except for four months last spring when she was on leave from the University. One undergraduate, Mr. Carey Lisse, has been supported part-time this fall by DOE funds. He is presently working on LEED data analysis.

Work supported by the DOE during the past year has resulted in the publication of two manuscripts, with a third currently under consideration. Copies of each of these papers are included. In addition, two other papers have been published and a third is in press which acknowledge support of the DOE, mainly in the form of equipment purchased for use in the studies described in this progress report. Copies of these papers are also included. Our work toward the objective of understanding the mechanism of chemical poisoning of small molecule decomposition reactions on clean and poisoned molybdenum and cobalt surfaces has been promising and productive on all fronts.

References

1. M. G. Lagally and M. B. Webb, Surface Sci. 35, 117 (1973).
2. L. J. Clarke, Surface Sci. 80, 32 (1979).
3. A. Ignatiev, F. Jona, H.-D. Shih, D. W. Jepsen, and P. M. Marcus, Phys. Rev. B11, 4787 (1975).
4. G. B. Olszewski and S. L. Bernasek, "Constant Momentum Transfer Averaging LEED Analysis of the Clean Mo(001) Surface," submitted to Phys. Rev. B; "Application of CMTA Analysis of LEED Data to Surface Structure Analysis: Experimental and Structure Reliability Considerations," proceedings of the IBM Conference on the Determination of Surface Structure by LEED, in press.
5. CAVLEED, as developed and modified by J. Pendry was supplied by Dr. Shih. The set of LEED programs described in Surface Crystallography by LEED, by H. Y. Tong and M. A. Van Hove was supplied by Dr. Van Hove.
6. D. L. Adams, H. B. Nielsen, and M. A. Van Hove, Phys. Rev. B20, 4789 (1979).
7. L. Eno and H. Rabitz, J. Chem. Phys. 72, 2314 (1980).
8. G. B. Olszewski and S. L. Bernasek, "Application of CMTA Analysis of LEED Data to Surface Structure Analysis. Experimental and Structure Reliability Considerations," proceedings of the IBM Conference on the Determination of Surface Structure by LEED, 1980, in press.

Bibliography of Project Publications

1. G. B. Olszewski and S. L. Bernasek, "Theoretical Scattering Amplitudes for the Atomic Scattering of Low-Energy Electrons for Use in Surface Crystallography by Low Energy Electron Diffraction." J. Appl. Cryst. 14, XXX (1981).
2. G. B. Olszewski and S. L. Bernasek, "Application of CMTA Analysis of LEED Data to Surface Structure Analysis. Experimental and Structure Reliability Considerations," proceedings of the IBM Conference on the Determination of Surface Structure by LEED, June, 1980, in press.
3. G. B. Olszewski and S. L. Bernasek, "Constant Momentum Transfer Averaging Analysis of the Clean Mo(001) Surface," submitted to Phys. Rev. B.
4. M. A. Langell and S. L. Bernasek, "Transition Metal Compound Surfaces I. The $\text{Na}_x\text{WO}_3(100)$ Surface." J. Vac. Sci. Technol. 17, 1287 (1980).
5. M. A. Langell and S. L. Bernasek, "Transition Metal Compound Surfaces II. The $\text{WO}_3(100)$ Surface." J. Vac. Sci. Technol. 17, 1296 (1980).
6. M. A. Langell and S. L. Bernasek, "High Energy Electron Loss Spectroscopy of $\text{WO}_3(100)$ and $\text{Na}_x\text{WO}_3(100)$ Single Crystal Surfaces," to be published in Phys. Rev. B.