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AUTOMATED ARXPS GONIOMETER/DIFFRACTOMETER

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ABSTRACT

This award provided for an automated computer-controlled goniometer/ diffractometer/manipulator with hot and cold stages and data acquisition system that was interfaced with the high resolution Scienta ESCA-300 X-ray photoelectron spectrometer at Lehigh University. The automation allows angular dependent X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) data to be accurately and rapidly collected without the very time-consuming and labor-intensive manual method that was previously required. It also provides for automated multi-sample analyses, collecting both wide survey scans and selected binding energy range analyses, with complete computer control and data storage. This allows 24 hr data collection without requiring the continuous presence of operators. The overall result is a greater productivity for the XPS laboratory, approximately doubling the output of the laboratory. While the automated computer-controlled goniometer/manipulator with hot/cold stage has benefitted other research groups at Lehigh University and both academic and industrial groups from outside the university, the principal utility of the facility for our research group has been for analyses of catalysts. Materials studied include both industrially significant dispersed and supported catalysts and model microcrystalline or single crystal catalysts. The automation of the angularly resolved XPS (ARXPS) and UPS (ARUPS) data collection greatly enhances the precise determination of surface structure and valence band structure of catalytically active materials and of adsorbates. We appreciate U.S. Department of Energy support and sponsorship for this unique facility.

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FINAL REPORT

BACKGROUND

This award provided the funding to obtain the automated goniometer/diffractometer/ manipulator that was attached to the analysis chamber of the Scienta ESCA-300 X-ray photoelectron spectrometer (XPS) located in the Zettlemoyer Center for Surface Studies at Lehigh University. The high resolution (energy, angle, and spatial) Scienta ESCA-300 XPS instrument, described in detail elsewhere [1], was obtained in part with funding from a 1987 DOE grant (U.S. DOE-URIP Grant No. DE-FG02-87ER75370). The U.S. DOE funds were matched nearly 4:1 from other sources, and the instrument is still the only one of its kind in the United States.

The instrument was developed and constructed by researchers from the Department of Physics of the University of Uppsala and Scienta Instrument AB, both located in Uppsala, Sweden. The design features of the instrument that was delivered to Lehigh University in January 1990 were partially modified by joint cooperation between us and the researchers in Sweden. This was aided by sabbatical leaves spent in Uppsala, Sweden by Kamil Klier, Gary W. Simmons, and Alfred C. Miller during the instrument design, construction, and testing/shakedown periods, during which partial support for research and travel was provided by a NSF US-Sweden Cooperative Research Grant (INT-8822746) to Gary W. Simmons.

During the following few years, we demonstrated the scientific principles, methodology, and theoretical interpretation of X-ray photoelectron diffraction (XPD) and ARXPS and ARUPS valence band measurements obtained by tedious and time-consuming manual manipulation of tilt (polar) and azimuthal angles [2-5]. These studies built upon our previous and ongoing work investigating the surface states of materials, especially Pd single crystals as models for Pd catalysts, and the surface chemistry of adsorbates, principally using low energy electron diffraction (LEED) and electron energy loss spectroscopy (EELS) coupled with temperature programmed desorption (TPD) [6-16]. We also demonstrated the sensitivity and resolution of the instrument in determining the state of interfaces in materials and the chemistry that occurs at these interfaces [9,17-24]. The computer-controlled automation expanded the capabilities and capacity of the Scienta ESCA instrument for conducting such fundamental studies, as well as automated data collection of XPS spectral data from a wide variety of materials extended from dispersed metal oxide and metal sulfide catalysts to polymer films, polymeric fibers, and resins to metals.

INSTRUMENTATION OBTAINED

An itemized list of the components of the instrumentation is given here, and a further description of the instrumentation and its capabilities is given in the next section of this report.

Automated Goniometer/Manipulator. A Seiko precision rotary drive with 5-axis computer-controlled motorized motion in the x, y, and z directions and with tilt and azimuthal rotations. It includes 15 m fiber optic RS232 communications system and Scienta

software for control of the stepping motors *via* a control computer that was provided by cost-shared funds.

New Imaging Board for the Electrostatic Lens. A new imaging board for the existing lens system was obtained, which provided for an appreciably higher spatial resolution to be achieved during analyses.

Improved Multi-Detection System. An improved microchannel plate (MCP)/CCD signal detection system was obtained with cost-shared funds, and this new technology has resulted in a factor of 5-10 increase in count rates. This allowed for a significant reduction in data collection time and improved sensitivity.

Heating/Cooling Facility. Two new stages were obtained that included new stub holder systems, a power supply, and temperature control and monitoring system. One stage is a cold stage (liquid nitrogen) and the other stage is a hot stage (resistive heating), and both provide stable temperature control in a high vacuum environment.

DESCRIPTION OF INSTRUMENTATION

The automated goniometer consists of an attachment on the side of the high vacuum analysis chamber and provides for computer-controlled motorized motions of x, y, and z translations and both polar (tilt) and azimuthal rotations. The range of motion is x = 50 mm and y, z = ±12.5 mm, with 3μm repeatability. For rotation of samples, the range for tilt rotation is -5 to 185° with 0.2° repeatability, while the range for the azimuthal rotation is ±185° with <1° repeatability. The system has fiber optic communication and dedicated software for computer control of the stepping motors.

To facilitate surface preparation and modifications, the specimens can be mounted on either of two analysis stages. The two stages hold a wide variety of custom designed movable stubs that hold the samples to be analyzed. The stubs allow the specimens to be moved to either of two pretreatment/treatment chambers, e.g. reduction in flowing hydrogen, ion sputtering, or surface modification with dopants such as Cs atoms. The main stage consists of a hot stage having a controlled heating capacity to 600°C. A cold stage is also now available that provides specimen temperature down to ≈-150°C, which allows surface stabilization of adsorbed molecules.

Further enhancement of spatial resolution is obtained by an up-graded electrostatic lens system that is centered on a new imaging board. This allows x-y elemental chemical state mapping with about 10-15 μ edge resolution. In addition to this, the advanced MCP/CCD detection system significantly increased (x10) counting efficiency with a concomitant decrease in data acquisition time. Both of these improvements significantly increased the performance of the Scienta ESCA-300 instrument.

Automation of the ARXPS and ARUPS data collection greatly enhanced the precise determination of surface structure (to within 0.2 nm of the surface) and of the subsurface layers (2-4 nm below the surface), as well as of the valence band structure of catalytically active materials and of adsorbates. Facilitated by the improved spatial electron optics of the Scienta instrument, it is possible to carry out ARXPS and ARUPS studies on ≥25 μm microcrystals. In addition, with the manipulator allowing computer-controlled motorized motion in the x-direction of 50 mm, it is easy to mount multiple samples on a specially designed stub, e.g. four powdered catalyst samples held in sample wells on a stub consisting

of an Al bar, and collecting complete spectral data sets (survey spectra and selected binding energy ranges) overnight. In addition, with motion in the y-direction of up to 25 mm, a double row of samples can be mounted on a single stub, e.g. 12-16 catalyst pellets mounted in two rows of 6 or 8 samples. Again, complete spectral data sets are collected by automated operation, and again multiply scans of each spectral range can be carried out to decrease background and increase the sensitivity of detection.

USERS OF THE INSTRUMENTATION

In addition to Lehigh University faculty in many academic departments using the goniometer/diffraction/manipulator system for XPS analyses of their samples, scientists from approximately 40 U.S. industrial laboratories and other universities have employed this system for surface analyses. At Lehigh University, faculty, research scientists, visiting scientists, postdoctoral research associates, graduate students, and undergraduate students carry out their own hands-on research using the automated XPS instrument. Dr. Alfred C. Miller provides guidance and instructs the users of the instrument by holding at least two classes each year. Several industrial scientists have been trained to operate the instrument and to personally carry out the analyses of their samples.

PUBLICATIONS

The publications by our research group to-date that are based wholly or in part on analyses using the enhanced XPS instrument with the automated goniometer/diffraction/ manipulator system are given below. Copies of these publications are available upon request. Other manuscripts are in preparation.

- "A Self-Modeling Approach to the Resolution of XPS Spectra into Surface and Bulk Components," Simmons, G. W., Angst, D. L., and Klier, K.; to be submitted.

- "Adsorption of Pentamethylcyclopentasiloxane on the Pd(100) Surface Studied by High Resolution X-Ray Photoemission Spectroscopy," Park, K. T., Herman, R. G., and Klier, K., Surf. Sci. Lett.; submitted.

- "Interaction of Tetrachloroethylene with Pd(100) Studied by High Resolution X-Ray Photoemission Spectroscopy,", Park, K. T., Klier, K., Wang, C.-B., and Zhang, W. X., J. Phys. Chem., **101**, 5420-5428 (1997).

- "Surface Acidity (Brønsted and Lewis) by High Resolution X-ray Photoelectron Spectroscopy," Johansson, M. and Klier, K., Topics Catal., **4**, 99-108 (1997).

- "Oxygen-Induced Surface Core Level Shift and Angle Resolved X-Ray Photoemission Spectroscopy (ARXPS) of c(2x2)O/Pd(100)," Park, K. T., Simmons, G. W., and Klier, K., Surf. Sci., **367**, 307-320 (1996).

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