Electronic Structure and Reactivity of Metal Surfaces

NATO ADVANCED STUDY INSTITUTES SERIES

A series of edited volumes comprising multifaceted studies of contemporary scientific issues by some of the best scientific minds in the world, assembled in cooperation with NATO Scientific Affairs Division.

Series B: Physics

RECENT VOLUMES IN THIS SERIES

Volume 7 – Low-Dimensional Cooperative Phenomena
edited by H.J. Keller

Volume 8 – Optical Properties of Ions in Solids
edited by Baldassare Di Bartolo

Volume 9 – Electronic Structure of Polymers and Molecular Crystals
edited by Jean-Marie André and János Ladik

Volume 10 – Progress in Electro-Optics
edited by Ezio Camatini

Volume 11 – Fluctuations, Instabilities, and Phase Transitions
edited by Tormod Riste

Volume 12 – Spectroscopy of the Excited State
edited by Baldassare Di Bartolo

Volume 13 – Weak and Electromagnetic Interactions at High Energies
(Parts A and B)
edited by Maurice Lévy, Jean-Louis Basdevant,
David Speiser, and Raymond Gastmans

Volume 14 – Physics of Nonmetallic Thin Films
edited by C.H.S. Dupuy and A. Cachard

Volume 15 – Nuclear and Particle Physics at Intermediate Energies
edited by J. B. Warren

Volume 16 – Electronic Structure and Reactivity of Metal Surfaces
edited by E. G. Derouane and A. A. Lucas

Volume 17 – Linear and Nonlinear Electron Transport in Solids
edited by J.T. Devreese and V. van Doren

The series is published by an international board of publishers in conjunction with NATO Scientific Affairs Division

A	**Life Sciences**	Plenum Publishing Corporation
B	**Physics**	New York and London
C	**Mathematical and Physical Sciences**	D. Reidel Publishing Company Dordrecht and Boston
D	**Behavioral and Social Sciences**	Sijthoff International Publishing Company Leiden
E	**Applied Sciences**	Noordhoff International Publishing Leiden

Electronic Structure and Reactivity of Metal Surfaces

Edited by
E. G. Derouane and A. A. Lucas
Facultés Universitaires N. -D. de la Paix
Namur, Belgium

PLENUM PRESS • NEW YORK AND LONDON
Published in cooperation with NATO Scientific Affairs Division

Library of Congress Cataloging in Publication Data

Nato Advanced Study Institute on Electronic Structure and Structure and Reactivity of Metal Surfaces, Facultés universitaires Notre-Dame de la Paix, 1975.
Electronic structure and reactivity of metal surfaces.

(NATO advanced study institutes series: Series B, Physics; v. 16)
Includes index.
1. Surface chemistry–Congresses. 2. Metallic surfaces–Congresses. 3. Chemisorption–Congresses. 4. Catalysis–Congresses. 5. Reactivity (Chemistry)–Congresses. I. Derouane, E. G. II. Lucas, A. A. III. Title. IV. Series.
QD506.AlN37 1975 546'.3 76-10692
ISBN-13: 978-1-4684-2798-1 e-ISBN-13: 978-1-4684-2796-7
DOI: 10.1007/978-1-4684-2796-7

Lectures presented at the NATO Advanced Study Institute on
Electronic Structure and Reactivity of Metal Surfaces held at
The Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium,
August 31-September 13, 1975

A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

United Kingdom edition published by Plenum Press, London
A Division of Plenum Publishing Company, Ltd.
Davis House (4th Floor), 8 Scrubs Lane, Harlesden, London, NW10 6SE, England

Foreword

What's new since Langmuir ?

Imagine that a young physicist would approach a granting agency and propose to contribute to heterogeneous catalysis by studying the heat conductivity of gases in contact with a hot filament. How would he be received now ? How would he have been treated sixty years ago ?

Yet, more than sixty years ago, Irving Langmuir, through his study of heat transfer from a tungsten filament, uncovered most of the fundamental ideas which are used to-day by the scientific community in pure and applied heterogeneous catalysis. Through his work with what were for the first time "clean" metal surfaces, Langmuir formulated during a period of a little over ten years until the early thirties, the concepts of chemisorption, monolayer, adsorption sites, adsorption isotherm, sticking probability, catalytic mechanisms by way of the interaction between chemisorbed species, behavior of non-uniform surfaces and repulsion between adsorbed dipoles.

It is fair to say that many of these ideas constituting the first revolution in surface chemistry have since been refined through thousands of investigations. Countless papers have been published on the subject of the Langmuir adsorption isotherm, the Langmuir catalytic kinetics and the Langmuir site-exclusion adsorption kinetics. The refinements have been significant. The original concepts in their primitive or amended form are used everyday by catalytic chemists and chemical engineers all over the world in their treatment of experimental data, design of reactors or invention of new processes.

On the other hand, during the past ten years, a second revolution has taken place in surface chemistry, especially that concerned with metallic surfaces. Technological advances have taken place in ultra-high vacuum technique, physical instrumentation affecting old methods such as low energy electron diffraction. New ways to look at photoelectron spectroscopy have evolved. Progress in solid state theory and computing has been made. As a result, new

concepts have emerged or are emerging which are essentially non-Langmuirian. Their effect on the science of chemical reactivity of surfaces will be profound. The new surface chemistry or physics or chemical physics is particularly vital in the countries disposing of an aggressive industry which equips the scientific worker with new instruments and ever faster computers.

It seems most timely to survey such advances in a didactic manner during an international meeting grouping the countries where this new revolution has taken place and in a leisurely way through the physics and chemistry, the theory and practice of metallic surfaces. The limitation to metals, wisely decided by the organizers of the NATO Institute whose proccedings follow, is not fundamental. It is just a reflection of reality as much of the new work deals at the moment with metallic surfaces.

What are the new concepts ? The list depends very much on what part of the surface science he is considering. I am suggesting here a few which are of considerable importance in heterogeneous catalysis where most of the current important applications of surface science can be found. First, from the large number of ordered structures on single crystal metal surfaces following chemisorption of atoms and molecules, the idea of island or patch chemisorption has emerged with attractive interactions between chemisorbed species. Second, the Langmuirian picture of site-exclusion kinetics in chemisorption has been modified significantly by the frequent mechanism of chemisorption through precursor states. Third, the idealized concept of adsorption sites has been relaxed in two important ways through surface reconstruction and through adsorption of compressed layers forming coincidence overlayer lattices. Fourth, the rigid band theory of alloys which dominated alloy catalysis in the fifties and sixties has been largely abandoned as a result of new findings in photoelectron spectroscopy. Fifth, many binding states of a given species exist even on a single crystal face.

The challenge to-day is that many of the simple ideas have been replaced by a wealth of new observations without consistent pattern or new guiding principles. If surface reconstruction does occur, when is it expected, both in the absence or in the presence of what impurities ? If the Pauling theory of the metallic bond with its convenient percentage d bond character is inadequate, what should we use instead to explain patterns of catalytic activity ? If attractive as well as repulsive forces between chemisorbed species are important, when do we guess that attraction will overwhelm repulsion ? If many binding states exist for a given species on a certain metal, which ones are important in a given process ?

But there is another challenge which faces the contemporay catalytic chemist as well as the theoretical and experimental physicist. Many catalytic metals and alloys are used in form of very

small particles, called clusters if most of the atoms in them are exposed to the surface. What are the properties of these clusters ? Their phase diagram ? Their superparamagnetic by opposition to ferromagnetic beavior ? Their surface composition in the case of alloys ? Their interaction with the support or carrier which preserves their existence ? Their electronic structure insofar as it differs from that of larger aggregates ? Their anomalous and mobile atomic structures ?

It is my guess that the third revolution in surface chemistry will deal with these small particles. They may well be easier to tackle theoretically than large crystals but they are certainly elusive objects for the experimental scientist. Yet many of the emerging tools of surface physics can be used in their investigation e.g. Mössbauer Spectroscopy, Extended X-ray Absorption Fine Structure and Small Angle X-ray Scattering. I have summarized elsewhere some of the recent catalytic results involving such object, as illuminated by recent results in surface science (1,2,3). Readers of this book who look for applications of their brand of surface science to heterogeneous catalysis may find in these references some facts to bolster their justification, if they need one, for studying the electronic structure of metals.

M. Boudart

Stanford, November 1975

(1) Chemisorption During Catalytic Reaction on Metal Surfaces. J. Vac. Sci. Technol., Vol. 12, No.1 (1975) (M. Boudart)

(2) "Concepts in Heteregeneous Catalysis", in "Interactions on Metal Surfaces", R. Gomer, Ed., Chapter 7, Springer Verlag, New York 1975 (M. Boudart)

(3) "Heterogeneous Catalysis", Chapter 7 in Volume 7 of Physical Chemistry : An Advanced Treatise (Eds.: H. Eyring, W. Jost, and D. Henderson), Academic Press 1975 (M. Boudart)

Preface

The lectures collected in this volume were presented at the NATO Advanced Study Institute on "Electronic Structure and Reactivity of Metal Surfaces" which was held at the Facultés Universitaires Notre-Dame de la Paix in Namur from August 31st to September 13th, 1975.

As indicated by its title, the initial purpose of the Institute was to provide a progressive and comprehensive course on fundamental problems in the physics and chemistry of metal surfaces with emphasis on their electronic structure, adsorptive, catalytic and reactivity behaviours.

The possibility for the attendence to familiarize itself with such basic properties of metal surfaces was made particularly timely by the all too persistent divorce between the languages used by surface physicists and surface chemists in this field and also by the highly relevant nature of the subject for our present day energy problems. It is hoped that the school and the present proceedings will help in bridging the two point of views by preparing some younger scientists to work and contribute in this most important field of surface physical chemistry.

The ordering of the lectures in this book closely follows the actual timetable of the Institute. The material is divided into four part.

First, a general introduction provides a critical overview of the field.

Second, the various theoretical physics and quantum chemistry approaches to the electronic structure of bare metal surfaces and chemisorption systems are presented.

The third part describes theoretical and experimental aspects of physical techniques for the investigation of the metal-gas interface.

The last part is devoted to more specific problems of metal surface reactivity and other catalytic properties. The present proceedings also list the short communications which were presented in addition to the main lecture programme.

All lecturers are to be complimented and thanked for the clarity of both their oral and written contributions.

We wish to express our deepest gratitude to the Scientific Affairs Division of NATO, the main sponsor of this Institute, and to the Facultés Universitaires de Namur and their Academic Authorities who gave us a generous financial help as well as all accomodation supports for the School.

We are particularly indebted to Prof. J.-M. André, our Scientific Secretary, who provided us with his invaluable experience in setting up the Study Institute.

A meeting of this size and length does not succeed without offering a lively social program to the participants and accompanying people. We are much obliged to Mr. G. Kelner of our public relation office who fulfilled this responsibility with inexhaustible imagination and we acknowledge the gracious help of Mrs Derouane, Mrs Lucas and Mrs J.-M. André for entertaining the ladies.

The secretarial burden fell on Miss P. Lonnoy who, throughout the Institute up to the final preparation of these proceedings, worked expertly and smilingly. We wish to thank her most heartedly.

Finally we gratefully acknowledge the further help to all the other people, hostesses, members of the Chemistry Department, students, etc. who took an active and usefull part in arranging many practical details during the Institute.

E.G. DEROUANE

A.A. LUCAS

Namur, November 1975

Contents

PART III - THEORETICAL AND EXPERIMENTAL ASPECTS OF PHYSICAL TECHNIQUES FOR THE INVESTIGATION OF THE METAL-GAS INTERFACE

PART IV - REACTIVITY AND CATALYTIC ACTIVITY OF METAL SURFACES