CATALYST SURFACE: PHYSICAL METHODS OF STUDYING

MINACHEV SHPIRO

> ADVANCES IN SCIENCE AND TECHNOLOGY IN THE USSR

Catalyst Surface: Physical Methods of Studying

Edited by KH. M. MINACHEV and E. S. SHPIRO Translated from the Russian by G. Leib

Mir Publishers Moscow

CRC Press
Boca Raton Ann Arbor Boston

Library of Congress Cataloging-in-Publication Data

Catalyst surface: physical methods of studying / edited by Kh. M. Minachev and E. S. Shpiro.

p. cm.--(Advances in science and technology in the USSR. Chemistry series)

Translated from the Russian.

Includes bibliographical references and index.

ISBN 0-8493-7532-0

1. Catalysts. 2. Surfaces (Technology) 1. Minachev, Kh. M. (Khabib Minachevich) II. Shpiro, E. S. III. Series.

QD505.C3866 1990

541.3'95—dc20

90-46126

CIP

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

© Mir Publishers, 1990

This edition published by CRC Press, Inc., 2000 Corporate Blvd. N.W., Boca Raton, Florida.

International Standard Book Number 0-8493-7532-0

Library of Congress Card Number 90-46126 Printed in the United States Catalyst Surface: Physical Methods of Studying Advances in Science and Technology in the USSR

Chemistry Series

此为试读,需要完整PDF请访问: www.ertongbook.com

PREFACE

New production processes involving catalysts can only be created at present when comprehensive specifications of a catalyst are available and the mechanism of their action is understood in detail. This is because the industry now puts stricter requirements on catalysts to ensure their selectivity, ecological cleanliness, and low energy and material costs. Our hopes that these expectations will come true are based on two positive trends in science and engineering, namely, the development of production processes to synthesize novel materials with controllable physicochemical properties, and the development and employment of physical methods (primarily for surface analysis) to completely characterize material at the molecular and atomic levels.

The 1970's saw substantial progress in studying the structure of the surfaces of model catalytic systems (single crystals and thin films) and their interaction with reacting molecules with the aid of physical methods of surface analysis. The progress in studying real catalysts (including industrial ones) has not been so great, and their development remains empirical. In the 1980's, the gap in our understanding the action of simulated and real catalytic systems has begun to shrink owing to the more comprehensive studying of real systems by a set of modern physical techniques that has been developed theoretically and methodologically. For example, at our laboratory alone, over 50 studies involving the analysis of catalyst surfaces by electron emission spectroscopy (EES) and ion spectroscopy (IS) have been completed in recent years. The total number of publications in this field has exceeded 1000. The goals of the studies have changed appreciably. In addition to solving some particular problems, they are aimed at establishing a fundamental relation between surface and catalytic properties.

This is why the reviews of catalyst surface analysis performed by physical techniques in the late 1970's and early 1980's [see, for example, A. W. Czanderna (ed.). *Methods of Surface Analysis*. New York: Elsevier (1975); J. Thomas and R. Lambert (eds.). *Characterization of Catalysts*. Chichester: Wiley (1980); and the monograph: Kh. M. Minachev, G. V. Antoshin, and E. S. Shpiro. *Fotoelektronnaya spektroskopiya i ee primenenie v katalize* (Photoelectron Spectroscopy and Its Use in Catalysis). Moscow: Nauka (1981)] no longer reflect the present state of this impetously developing field of science. All this prompted us to attempt a newer and deeper analysis and overview of studies of catalyst surfaces by EES and IS, chiefly on the basis of our own results, and also of data that appeared in Soviet and foreign publications after 1980.

In addition to new results, the present monograph briefly sets out the fundamentals of the techniques used and the methodology of studying real catalytic systems. We hope our foreign readers will be interested in the work of Soviet authors and be able to appraise their contribution to the development of this important field of surface and catalysis physical chemistry.

Kh. Minachev, E. Shpiro

CONTENTS

Introduction Physical Fundamentals of Electron Emission and Ion Spectroscopies 17 1.1 Photoelectron Spectroscopy 17 1.1.1 Chemical Shifts and Width of Core Level Lines. Shape of Valence Bands 18 1.1.2 Structure of the Core Level Spectra 22 1.1.3 Intensities of Photoelectron Spectra 24 1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46 1.4 Other Surface Science Techniques 49	List of Abbre	eviations 9		
1.1 Photoelectron Spectroscopy 17 1.1.1 Chemical Shifts and Width of Core Level Lines. Shape of Valence Bands 18 1.1.2 Structure of the Core Level Spectra 22 1.1.3 Intensities of Photoelectron Spectra 24 1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	Introduction	II		
1.1.1 Chemical Shifts and Width of Core Level Lines. Shape of Valence Bands 18 1.1.2 Structure of the Core Level Spectra 22 1.1.3 Intensities of Photoelectron Spectra 24 1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	1	Physical Fundamentals of Electron Emission and Ion Spectroscopies 17		
1.1.1 Chemical Shifts and Width of Core Level Lines. Shape of Valence Bands 18 1.1.2 Structure of the Core Level Spectra 22 1.1.3 Intensities of Photoelectron Spectra 24 1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	1.1	Photoelectron Spectroscopy 17		
 1.1.3 Intensities of Photoelectron Spectra 24 1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46 		Chemical Shifts and Width of Core Level Lines. Shape of Valence		
 1.1.3 Intensities of Photoelectron Spectra 24 1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46 	1.1.2	Structure of the Core Level Spectra 22		
1.1.4 UPS: Spectra of the Adsorbed State. Angle-Resolved Photoemission 30 1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	1.1.3			
1.2 Auger Electron Spectroscopy 31 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	1.1.4	Peter 17		
 1.3 Ion Spectroscopies 37 1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46 	1.2			
1.3.1 Ion Sputtering 38 1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	1.3			
1.3.2 Secondary Ion Mass Spectrometry 41 1.3.3 Ion Scattering Spectroscopy 46	1.3.1	The state of the s		
1.3.3 Ion Scattering Spectroscopy 46	1.3.2	AND 10 CONTRACTOR OF THE STATE		
	1.3.3			
1.7 Other burlace believe rechniques 77	1.4	Other Surface Science Techniques 49		
2 Instrumentation and Experimental Procedures 51	2	Instrumentation and Experimental Procedures 51		
2.1 Instrumentation 52	2.1	Instrumentation 52		
2.1.1 Electron Spectrometers 52	2.1.1	Electron Spectrometers 52		
2.1.2 Resolution and Sensitivity of Electron Spectrometers 56	2.1.2	Resolution and Sensitivity of Electron Spectrometers 56		
2.1.3 Excitation and Registration of Scattered Ion Spectra and Secondary Ion Mass Spectra 59	2.1.3	Excitation and Registration of Scattered Ion Spectra and Secondary Ion		
2.2 Basic Spectral Characteristics and Calibration of the Spectra 61	2.2			
2.2.1 XPS 61				
2.2.2 Other Techniques 67		Other Techniques 67		
2.3 Spectra Collecting and Processing 70				
2.3.1 Acquisition and Primary Processing of XPA Data 70				
2.3.2 Determining the Intensity and the True Lineshape 72				
2.4 Specimen Preparation, Transfer, and Treatment 76	2.4			
2.4.1 Preparation and Insertion of Specimens 76	2.4.1			
2.4.2 Preparation Chamber of the Spectrometer ES 200B 77	2.4.2			
2.4.3 A Reactor for High-Temperature Treatment of Catalysts under Atmospheric	2.4.3			
Pressure 79				
2.4.4 Transfer Glove Box 81	2.4.4	Transfer Glove Box 81		
2.4.5 Reactor with Catalyst Sampling 82	2.4.5	Reactor with Catalyst Sampling 82		
2.4.6 Preparation Chamber of Spectrometer XSAM 800 82	2.4.6			
2.4.7 System for Multifold Handling of Catalysts 84	2.4.7			
2.4.8 Measurement of Spectra in Different Stages of a Catalytic Reaction 85	2.4.8			
The Use of Electron Emission and Ion Spectroscopies for Studying the Fundamental Characteristics of a Surface 87	3			
3.1 Chemical State of Components and Electron Structure of Catalysts 88	3.1	Chemical State of Components and Electron Structure of Catalysts 88		
3.2 Electron State of Small Clusters and Surface Atoms 100				
3.3 Surface Composition 112				
3.3.1 Surface Segregation in Alloys 112				
3.3.2 Distribution and Dispersion of Components on Porous Supports 118				
3.3.3 Surface Segregation in Supported and Oxide Systems 125				
3.4 Structure of a Surface 127				

4	The Study of Heterogeneous Catalysts by Electron Emission and Ion Spectroscopies 133			
4.1	Metals and Allovs 134			
4.1.1	Electron Structure of the Surface of Metals and Alloys 136			
4.1.2	Platinum Alloys 140			
4.1.3	Other Solid Solutions and Intermetallics 143			
4.1.4	Bimetal Thin Films and Catalysts Based on Them 158			
4.1.5	Catalysts Based on Alloys, Intermetallics, and Their Hydrides 161			
4.2	Oxide Catalysts 167			
4.2.1	Electron Structure of Oxides. State of Oxygen 168			
4.2.2	Transition Metal Oxides 176			
4.2.3	Binary and Multicomponent Oxide Systems 181			
4.3	Zeolite Catalysts 185			
4.3.1	State of Components and Surface Composition of Starting and Modified			
	Zeolite Materials Containing No Transition Elements 187			
4.3.2	Cation and Reduced Forms of Zeolites with Transition Elements 199			
4.3.3	Metal Complexes in Zeolites 201			
4.3.4	Cations in Intermediate Oxidation States and Highly Dispersed Clusters 206			
4.3.5	State of Transition Elements and Surface Composition of Metal-High- Silica Zeolite Catalysts 211			
4.4	Oxides on Supports 217			
4.4.1	Supported Binary Oxides (Ni, Co, No, W) 218			
4.4.2	Ternary Ni-Mo, Co-Mo, and Ni-W Systems 227			
4.4.3	Chromium-Containing Catalysts 228			
4.4.4	Supported Rhenium Catalysts 230			
4.4.5	Copper-Containing Catalysts 233			
4.5	Supported Metals 238			
4.5.1	Formation of a Metal Phase in Supported Catalysts 239			
4.5.2	Electron State of Highly Dispersed Particles. Metal-Support Interaction 247			
4.5.3	Strong Metal-Support Interaction 255			
4.5.4	Effect of Strong Metal-Support Interaction for Model Catalytic Systems 258			
4.5.5	Effect of Strong Metal-Support Interaction for Real Highly Dispersed Catalysts 260			
4.5.6	Effect of Strong Metal-Support Interaction for Other Catalysts 267			
4.6	Bimetal Supported Catalysts 269			
4.6.1	Ensemble and Ligand Effects in Catalysis with Supported and Unsupport-			
	ed Alloys 270			
4.6.2	Physicochemical Characterization of Dispersed Supported Alloys 272			
4.6.3	Bimetal Supported Clusters 274			
4.6.4	Bimetal Platinum-Containing Catalysts 279			
5	Relation between the Characteristics of a Surface and Its Catalytic			
	Properties 287			
5.1	Catalysts Based on Alloys and Intermetallics 288			
5.2	Oxide Systems 292			
5.3	Zeolite Catalysts 300			
5.4	Supported Mono- and Bimetal Systems 312			
Conclusion 323				
References 325				
Author Index 353				
Subject Index 359				

LIST OF ABBREVIATIONS

AES Auger electron spectroscopy

ARUPS Angle-resolved ultraviolet photoelectron spectroscopy

ARXPS Angle-resolved X-ray photoelectron spectroscopy

CAT Constant analyzer transmission
CHA Concentric hemispherical analyzer

CMA Cylindrical mirror analyzer

CNDO Complete neglect of differential overlapping

CRR Constant relative resolution

DV Discrete variation

EES Electron emission spectroscopy

EHM Extended Hückel method ELS Electron loss spectroscopy

EPR Electron paramagnetic resonance

ESCA Electron spectroscopy for chemical analysis

EXAFS Extended X-ray absorption fine-structure spectroscopy

FABMS Fast atom bombardment mass spectroscopy

FAT Fixed analyzer transmission FEM Field emission microscopy FRR Fixed relative resolution

FWHM Full width at half maximum peak height

HREELS High resolution electron energy loss spectroscopy HRTEM High resolution transmission electron microscopy

IPS Inverse photoemission spectroscopy

IR Infrared spectroscopy
IS Ion spectroscopy

ISS Ion scattering spectroscopy

LCAO Linear combination of atomic orbitals

LEED Low-energy electron diffraction

LEELS Low-energy electron loss spectroscopy

MASNMR Magic angle spinning nuclear magnetic resonance

Me Metal

MO Molecular orbital

MSD Multi-channel solid detector

NEXAFS Near extended X-ray absorption fine-structure spectroscopy

NMR Nuclear magnetic resonance

PAX Photoemission of absorbed xenon

10 List of Abbreviations

PZC Point zero charge

RED Radial electron distribution

REM Rare earth metal(s)

SAM Scanning Auger spectroscopy (microprobe)

SCF Self consistent field

SEXAFS Surface-sensitive extended X-ray absorption fine-structure spec-

troscopy

SIMS Secondary ion mass spectrometry SMSI Strong metal-support interaction

SNIMS Secondary neutral ion mass spectrometry

SW Scattered wave

TDS Thermal desorption spectroscopy
TEM Transmission electron microscopy

TOF Turnover frequency UHV Ultrahigh vacuum

UPS Ultraviolet photoelectron spectroscopyXAES X-ray Auger electron spectroscopyXANES X-ray absorption near-edge spectroscopy

XAS X-ray absorption spectroscopyXPD X-ray photoelectron diffractionXPS X-ray photoelectron spectroscopy

XRD X-ray diffraction analysis

INTRODUCTION

The 1970's are customarily considered the beginning of a new stage in the fundamental studies of catalysis and in the prediction of the properties of various catalytic systems. This stage is characterized by the development of new ways of synthesizing catalysts ("heterogenized" complexes, materials with the structure of zeolites, etc.) and also by the application of experimental and theoretical techniques enabling one to describe the structure of a surface and the nature of gas-solid interaction. The use of techniques such as lowenergy electron diffraction (LEED), Auger electron spectroscopy (AES), and low-energy electron loss spectroscopy (LEELS) resulted in appreciable progress in understanding the catalytic action of atomically pure surfaces of metal single crystals [1, 2]. In particular, it became possible to explain the cause of the different structural sensitivity of reactions, establish the substantial contribution of the reaction medium to the formation of the "working" surface of a catalyst, and confirm the validity of a local approach when describing processes of adsorption and catalysis. At present, the entire set of techniques of the surface science is employed for this class of catalysts including the most up-to-date ones such as scanning tunneling microscopy. These techniques have a high surface sensitivity and provide information of the fundamental characteristics of solid surfaces, namely, the crystallographic and electron structure, the chemical state and local environment of elements, and the nature and geometry of the bond of the gas or liquid molecules to the solid. At present, we can list over fifty techniques and methods that were or are being used to study surfaces.

At the same time, to achieve real progress in the development of catalysts, it is essential to study the formation and nature of the activity of real catalytic systems with the aid of these techniques. Owing to fundamental restrictions, only some surface analysis techniques can be used for such investigations. The most effective techniques that have already recommended themselves in studying the surface of heterogeneous catalysts include electron emission spectroscopies (EES), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and ultra-violet photoelectron spectroscopy (UPS) (Table 1). They were first applied to catalysis at the beginning of the 1970's. Auger electron spectroscopy, especially during the first period, was employed for a qualitative and semi-quantitative analysis of the composition of metal and alloy catalyst surfaces. X-ray photoelectron spectroscopy [or electron spectroscopy for chemical analysis (ESCA)], developed in the fundamental and

Table 1. Characteristics of Electron Emission and Ion Spectroscopies

		Average	Average sensitivity			
	Basic information	concentration, %	mono- layer frac- tions	Depth of analyzed layer, nm	Local resolution, nm	Applicability to specimens with various electrophysical and structural characteristics
X-ray pho-	Valence state,					
oelectron	electron struc-					
ýc	ture, surface					Any specimens
(XPS)	composition	0.5-1.0	10^{-1}	2-4	104	
Ultra-vio-	Electron struc-					
let photo-	ture of surface,					
	nature and geo-					Conductors,
py	metry of adsorp-					semicon-
(UPS)	tion bond	1	10-1	1-2	ĺ	ductors
	Electron struc-					
	ture, surface					
by	composition,					
	depth profiles	0.05-0.1	10^{-2}	1-3	Ī	Ditto
(AES)						
Scanning	Surface composi-					
	tion of local					
	surface areas	0.1	10 - 1	1-3	20-50	Ditto
scopy (micro-						
probe) (SAM)						

Any specimens	Ditto	Single crystals, conductors and semiconduct-ors
50-	100	I
0.5°- 100 ^b	0.2- 0.3°	Í
10-3	10 - 2	10 - 3 - 10 - 2
0.01	0.1	ĺ
Fragments and local structure, composition of surface (semiquantitative analysis), depth profiles	Composition and structure of upper surface layers, depth profiles	Vibrational states of absorbed atoms and molecules, nature and geometry of adsorption bond
Secondary ion mass spectro- metry (SIMS)	lon scat- tering spectroscopy (ISS)	Low energy electron loss spectro-scopy (LEELS)

^aStatic mode.

^bDynamic mode, SIMS.

^cMonolayer.

applied works of Siegbahn's school [3-5], was found to be more universal. Owing to these works, the first high-resolution spectrometers were developed. A high sensitivity of XPS of the core levels was revealed when studying the electron structure of substances and chemical transformations. Although attention was also given earlier to the surface sensitivity of the technique, thorough investigations in this field began in the 1970's [6-28].

Let us consider the basic features of photoelectron spectroscopy that are especially important when studying adsorption and catalysis.

- 1. The effective escape depth of photoelectrons is determined by the mean free path up to inelastic collisions with a lattice (λ) and is within 2-4 nm. The attenuation of the signal of the photoelectrons is of an exponential nature. This suggests that the thickness of the layer being analyzed does not exceed 3λ , while about 60% of the intensity falls to the share of layer λ . Hence, surface layers less than 10 nm thick are analyzed by using XPS.
- 2. The energetic position of the inner level lines (or the chemical shift) characterizes the valence and coordination state of elements, the degree of ionicity of a bond or the effective charge, while the position, shape, and intensity of the valence bands characterize the energy of the valence orbitals and the density of the occupied states in the valence band.
- 3. The energy and angular distribution of the photoelectrons emitted from adsorbates reflect the type and geometry of an adsorption bond.
- 4. The intensity of the lines is the basis for a quantitative analysis of a surface.
- 5. The technique can be used to study all the elements of the periodic table except hydrogen.

In the late 1960's, the first publications also appeared describing the use in catalysis of techniques based on the interaction of 0.5-10-keV ions with a surface. The best known of them include secondary ion mass spectrometry (SIMS) and low-energy ion scattering spectroscopy (ISS) [6-8, 29, 30]. In both techniques, the surface of a specimen is bombarded by ions, most often of inert gases. In SIMS, the sputtered substance in the form of ions is analyzed, and in ISS — the primary ions that have spent their energy on elastic collisions with the substance. The main merits of SIMS is its high elemental sensitivity (Table 1) and the possibility of procuring data on the composition of the top and deeper layers. The main feature of ISS is its extremely high sensitivity to a surface — under definite conditions information is received from only the first layer of a specimen. It should be noted that owing to the difficulties involved in running experiments and interpreting their results, SIMS and ISS

Introduction 15

have meanwhile not been embodied to such an extent in catalysis as the electron spectroscopy techniques.

The main object of the present monograph is to consider the fundamentally new information that is given by EES and IS or will most likely be given when these techniques are further developed for understanding the mechanism of formation of active surfaces of various types of catalysts and the nature of their activity. Our readers can acquaint themselves with more particular data independently by turning to the references. A number of problems remain in each of the considered techniques whose solution requires their further theoretical and methodological development or the use of additional techniques. These problems include a quantitative description of the electron structure, quantitative analysis of the surface and near-surface layers of heterogeneous systems, improvement of the accuracy of the spectral parameters and their standardization for non-conducting specimens, and the development of procedures wherein the pretreatments of the specimens in situ and the simulation of a catalytic process are closer to real conditions. All these matters are dealt with in the present monograph.

We considered primarily the works including investigations of model and real objects, and employing not only EES and IS, but also such effective techniques as EXAFS, NMR in solids, and varieties of electron microscopy. It is just such works, in our opinion, that will allow one to understand more deeply the contribution of the collective and local properties of a surface to the proceeding of an elementary catalytic event and will be the foundation for building up a modern theory of the selection of optimum catalysts.

The present monograph has been conceived to be helpful not only for specialists, but also for a broad circle of scientists working in the field of the physical chemistry of surfaces and catalysis. Chapter 1 briefly treats the physical fundamentals of the EES and IS techniques that were used to obtain the main results. Since these questions were repeatedly considered in special monographs and reviews [3, 5, 8, 10, 30-34], the main attention in this chapter is devoted to the specific features of the analysis and interpretation of the spectra of complicated systems, a comparison of the possibilities of individual EES and IS techniques, as well as to other related techniques of surface analysis. Chapter 2 describes the procedure of an experiment with a view to the latest developments and discusses the problems of standardizing spectral data. Chapters 3-5 contain the results of studying catalysts by EES and IS. Here Chap. 3 on the example of the latest achievements reveals the possibilities of the techniques in studying the fundamental properties of a surface: the electron structure, chemical state of the components, and the composition, local

structure, and morphology of the surface. It also discusses the most important theoretical and methodological problems such as the electron structure of small metal clusters and the quantitative analysis of heterogeneous surfaces. Chapter 4 discusses in detail data on various types of catalysts, namely, metals and alloys, oxides, zeolites, and mono- and polymetallic supported catalysts. Chapter 5 gives examples of studying the formation of surfaces and the nature of the active centers of new and existing catalysts used in the most important processes of petroleum refining, petrochemistry, organic, and inorganic syntheses.