CATALYST SURFACE: PHYSICAL METHODS OF STUDYING

MINACHEV
SHPIRO

ADVANCES IN
SCIENCE AND TECHNOLOGY
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Edited by KH. M. MINACHEV and E. S. SHPIRO
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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

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

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 spectroscopy
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 spectroscopy
XAES	X-ray Auger electron spectroscopy
XANES	X-ray absorption near-edge spectroscopy
XAS	X-ray absorption spectroscopy
XPD	X-ray photoelectron diffraction
XPS	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 low-energy 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

Technique	Basic information	Average sensitivity		Depth of analyzed layer, nm	Local resolution, nm	Applicability to specimens with various electrophysical and structural characteristics
		concentration, %	monolayer fractions			
X-ray photoelectron spectrosopy (XPS)	Valence state, electron structure, surface composition	0.5-1.0	10^{-1}	2-4	10^4	Any specimens
Ultra-violet photoelectron spectroscopy (UPS)	Electron structure of surface, nature and geometry of adsorption bond	—	10^{-1}	1-2	—	Conductors, semiconductors
Auger electron spectroscopy (static) (AES)	Electron structure, surface composition, depth profiles	0.05-0.1	10^{-2}	1-3	—	Ditto
Scanning Auger spectroscopy (microprobe) (SAM)	Surface composition of local surface areas	0.1	10^{-1}	1-3	20-50	Ditto

Secondary ion mass spectrometry (SIMS)	Fragments and local structure, composition of surface (semi-quantitative analysis), depth profiles	0.01	10^{-3}	0.5[a]-100[b]	50-100	Any specimens
Ion scattering spectroscopy (ISS)	Composition and structure of upper surface layers, depth profiles	0.1	10^{-2}	0.2-0.3[c]	100	Ditto
Low energy electron loss spectroscopy (LEELS)	Vibrational states of absorbed atoms and molecules, nature and geometry of adsorption bond	—	10^{-3}-10^{-2}	—	—	Single crystals, conductors and semiconductors

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[a] Static mode.
[b] Dynamic mode, SIMS.
[c] Monolayer.

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 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.