EXPERIMENTAL METHODS IN CATALYTIC RESEARCH

VOLUME III

Characterization of Surface and Adsorbed Species

Edited by
Robert B. Anderson
and
Peter T. Dawson

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Characterization of Surface and Adsorbed Species

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PREFACE

In this century catalysis has advanced from a laboratory curiosity to a major component of the chemical and petroleum industries. Catalysis will play an equally important role in new processes for producing alternate fluid fuels. The development of catalysis was initially a mysterious art requiring laborious empirical testing. These tests will probably always be a part of catalyst development, but the process can be performed expeditiously by utilizing the vast store of scientific and practical information currently available and by employing modern research tools. Concurrent with practical developments, new research tools were applied to the investigation of catalysts and catalytic reactions. Some of these new experimental procedures were developed especially for catalysis, and others were adapted from chemistry and physics. The improved research tools and the concepts resulting from their use have dispelled many of the mysterious aspects of catalysis; however, they have disclosed a host of new and challenging problems. Since 1935 the experimental methods used in catalytic research have increased both in number and complexity, so that mastery of all of the techniques available is difficult.

In the 1960s, heated arguments over the relative merits of pure and applied (clean surface and dirty surface) research in advancing our understanding of catalysis were commonplace. In the 1970s these arguments have subsided as research workers came to appreciate the necessity for both approaches, and fewer experimentalists now remain entrenched at one end or the other of the spectrum of cleanliness. Furthermore, the elegant methods applied by the surface physicist to simple nonreactive systems are now becoming essential characterization tools of the applied catalytic laboratory. Volume III provides an account of these methods written by specialists in the area. As in Volume I, each chapter includes a description of the method and

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its fundamental principles, the apparatus used, the data obtained and their interpretation, and finally an account of special problems related to catalytic research. Volume II considers the preparation and examination of practical catalysts, and Volume III the characterization of surfaces and adsorbed species.

In the past decade we have seen the introduction to surface science of a very large number of powerful techniques for the characterization of surfaces and adsorbed species. To a greater or lesser extent these techniques are now being applied to investigations on catalysts and catalytic processes. Volume III provides a practical guide to these exacting experimental methods and their theoretical basis. Surface scientists have adopted convenient, but confusing, acronyms for their techniques (LEED, AES, PES, ESCA, FIM, etc.). Chapter 1 provides a useful overview of the plethora of surface spectroscopies and serves to orient the reader. The remaining chapters contain detailed accounts of the most useful of these techniques. The very short escape depth for electrons from solids makes them the most important probe for surface properties, both geometric and electronic. Chapter 2 describes the various electron spectroscopies that are rapidly becoming indispensable surface analytic tools. The application of low-energy electron diffraction to structure determination of surfaces is outlined in Chapter 3. Scattering techniques are becoming increasingly important, and Chapters 4 and 5 deal with ion and molecular beam scattering, respectively. The most utilized techniques for characterizing adsorbed species involve desorption of the adlayer by one of several different processes; these desorption methods are discussed in chapter 6. Finally, Chapter 7 contains an account of the current status of infrared spectroscopy as applied to surface studies.

Clearly no laboratory should find it difficult to select a surface characterization technique, appropriate to its problems and budget. However, it is widely accepted that an unambiguous description of a surface requires the application of several surface probes, preferably combined within a single experimental system.

The authors were asked to describe their specialty at a level understandable to a physical chemist with no experience in their field. These accounts were to provide an adequate introduction to both the experimental procedures and the theory. To a large degree these objectives have been accomplished. The editors have generally accepted the system of units chosen by the authors; these units are probably those that the reader will encounter in the current literature of that particular area.

The editors thank Drs. J. A. Davies, T. E. Madey, K. A. R. Mitchell, P. A. Redhead, and B. R. Williams for their helpful comments.

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1

INTRODUCTION TO SURFACE SPECTROSCOPIES*

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I. The Propst Diagram

Techniques for the spectroscopic analysis of solid surfaces have been spawned for the past decade in numbers that strain our capacity to devise new acronyms. Will this period of fecundity continue indefinitely, or is the end imminent, as one by one we exhaust all the possibilities? Some idea of the number of possibilities might be gained from a consideration of the well-known Propst diagram (Fig. 1). The circle represents the sample to be

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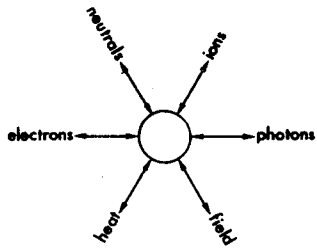

Fig. 1. The Propst diagram. The circle represents the sample to be analyzed. Ingoing arrows represent the various probes used to excite the sample. The possible responses to that excitation are indicated by the outgoing arrows, which convey information about the sample. Every spectroscopy can be represented by a combination of an arrow in and an arrow out. A single combination may, however, lead to several dissimilar spectroscopies, depending on what property of the probe and output are measured.

analyzed. Arrows going in correspond to the possible surface probes. Outgoing arrows correspond to the secondary particles, which convey information about the sample. Each combination of an arrow in and an arrow out would seem to constitute a potential analytical technique. There are, however, only 36 such combinations, all of which have been tried at some time, and about half of which are in more or less common use. Clearly there exist many more techniques than this.

The profusion of spectroscopies stems from the fact that a single combination or an arrow in and an arrow out may lead to several quite dissimilar spectroscopies, depending on what properties of the probe and the emitted particles are measured. The change in momentum of an electron elastically scattered from a surface, for example, can provide information on the arrangement of its atoms. The measurement of characteristic energy losses of scattered electrons, on the other hand, has produced information on such diverse phenomena as core level excitations, collective oscillations of the electron gas, and vibrational modes of surface atoms, depending on what energy range is involved. Thus the number of new possibilities seems almost unlimited. In addition, older techniques that have been tried and rejected will continue to be rediscovered as their limitations are obviated by advances in technology or the interpretation of their output is made possible by new theoretical models.

Many of the spectroscopies that have proven useful in surface science are reviewed in detail in the following chapters. In an introductory chapter it is possible to do little more than provide a catalog of techniques and stress those which best illustrate the underlying principles that unite this rich and varied field.

II. Scorekeeping

Order ranking surface spectroscopies would at best be an entertaining diversion, since each technique views the surface from a different perspective. Thus it is not possible to divorce the relative merits of surface spectroscopies from the problems they are expected to solve. There are, however, a number of parameters such as resolution and sensitivity that are common to all spectroscopies. Unfortunately the use of these parameters can be very treacherous. In the first place, they are to a large extent transmutable. One can, for example, usually trade sensitivity and resolution for bandwidth or nondestructiveness, over a wide range. The optimum trade-off between these parameters depends on what you are trying to learn. It is misleading, therefore, to specify the sensitivity of a technique without describing its relationship to the other parameters. Even then it may be difficult to distinguish the intrinsic limitations of a technique from the limitations of particular instruments and of the scientists who employ them: "In unskilled hands, a Stradivarius is just a fiddle."

A. Bandwidth and Statistical Noise

A unifying feature of the surface spectroscopies is their reliance on a vacuum environment. It is a marvelously unreactive environment, but from the standpoint of heterogenous catalysis, it leaves one with the problem of extrapolating from essentially static surface properties measured at pressures of perhaps 10^{-10} Torr to the dynamic conditions of the surface during reactions at much higher pressures. Surface scientists may, however, take satisfaction in the words of Big Daddy in the Tennessee Williams play *Cat on a Hot Tin Roof* that "A vacuum is a hell of a lot better than some of the stuff that nature replaces it with." Even at a pressure of 10^{-10} Torr a complete monolayer of contamination can condense on a surface in about two hours. It is the contamination rate that determines the maximum time constant that can be tolerated in a surface measurement.

The imposition of a finite time interval in which a measurement must be completed results in an unavoidable statistical uncertainty. This "shot effect" (*90*) is a consequence of the fact that the signal consists of discrete quanta. From Poisson's law, the shot effect can be expressed in terms of the signal-to-shot-noise ratio S/N_s as

$$S/N_s = (\sigma IT)^{1/2} \tag{1}$$

where T is the measurement time, I the rate at which the sample is probed, and σ the number of signal events counted per probe event. The burst of electrons produced by a single particle striking a multiplier, it should be

noted, constitutes a single signal event. The purpose of the multiplier is just to ensure that every signal event can be counted. The output pulses are not of uniform size, however, and if the pulses are integrated rather than counted, additional noise is introduced by the multiplier, depending on the moments of the pulse height distribution (*99*).

The shot effect produces a white noise spectrum, which is to say, its contribution depends only on the bandwidth (reciprocal of the measurement time constant T). In principle, any signal-to-shot-noise ratio can be achieved by increasing I or T. There are, of course, practical limits on how large I can be made, just as the measurement will be corrupted if T becomes an appreciable fraction of the monolayer contamination time.

There is an unfortunate tendency to equate an increase in achievable bandwidth with an increase in sensitivity. The sensitivity of a surface analytical technique is properly stated in terms of the smallest fraction of a monolayer on which a meaningful measurement can be made. Harris (*37*), for example, first estimated the sensitivity of electron-excited Auger spectroscopy at one-tenth of a monolayer. Improvements in the technique since that time have increased the achievable bandwidth by perhaps three orders of magnitude (as compared to at least seven orders that one might expect by laying the claims made for each improvement end to end). Each increase in bandwidth has been hailed as an increase in sensitivity [see, for example, Palmberg *et al.* (*74*)], but a comparison of recent Auger spectra with those taken by Harris makes it clear that the dramatic increase in the achievable speed of the technique has not been accompanied by a proportionate increase in achievable sensitivity. What then limits sensitivity?

B. Sensitivity and Background

In a paper that provided the foundation for a new field of study, Lander (*52*) established the presence of Auger electron emission peaks in the secondary emission spectra of electron-bombarded surfaces and described the principal factors determining their shape.* Unfortunately, Auger electrons comprise only a tiny fraction of all secondary electrons, and electron-excited Auger electron spectroscopy (EEAES) did not appear to offer a sensitive method of surface analysis. Fifteen years later, however, Harris (*37*) demonstrated that by the simple expedient of taking the derivative of the secondary emission spectrum, the Auger emission features could be greatly enhanced. Harris was simply exploiting the fact that the Auger features are distinguished from most of the remainder of the secondary

*Two years earlier, Steinhardt and Serfass (*98*) described a practical Auger spectrometer utilizing X-ray excitation.

electron spectrum by their relative sharpness. Every spectroscopy relies on some such distinguishing characteristic to sift the desired signal from a background of unwanted emissions that the probe has indiscriminately stimulated.

The sensitivity of every analytical technique is ultimately limited by a residue of background that is in some way correlated with the desired signal. If we increase the primary current, the background, unlike the shot noise, will increase in direct proportion to the signal. Let us suppose, however, that we are free to reduce arbitrarily the statistical noise contribution by increasing indefinitely the measurement time. Does this mean we can in principle detect any signal, however small, on top of the background? Unhappily, the answer is no. *If a scientist exercises unlimited patience in making a measurement, something will go wrong before he finishes.* This phenomenon, familiar to every experimentalist, is appropriately named the "flicker effect."

A great deal has been written on the sources of low-frequency or flicker noise. In vacuum tube amplifiers it has been attributed to work function variations produced by the diffusion of material over the surface of the emitter (*103*). In solid state amplifiers it is usually associated with the existence of "slow" surface states (*62*). More generally, however, the signal-to-flicker-noise ratio can be regarded as a measure of the stability of the entire measurement system. In contrast to the white-noise spectrum resulting from shot effect or from thermal noise in the measurement circuit (*46*), flicker noise is described by a $1/f$ spectrum. Thus it increases in direct proportion to the time required for the measurement. It is a little like trying to measure the width of a highway with a meter stick; the more carefully you try to make the measurement, the greater the probability that you will be run over by a truck before you finish.

The effect of a background level is to amplify the flicker noise. Small changes with time in any measurement parameter may completely obliterate a signal in the presence of a large background. Increasing sensitivity is thus equivalent to suppressing the low-frequency Fourier components of the spectrum. Simply subtracting the background, regardless of the sophistication with which it is done (*40*, *95*), may simplify analysis of the spectrum, but it does nothing to increase sensitivity.

C. Resolution and the Instrument Response Function

Any cosmetic that is applied to a spectrum to cover the blemishes of noise may also obscure physical information. Nature fortunately provides us with fairly clear limiting goals for the resolution of our instruments. In the case of core level spectroscopies, for example, there is little purpose in being able

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