

altered. Studies of crystallization kinetics from the pure melt show that the level of crystallinity attained decreases with increasing molecular weight.³⁶ Thus, the level of crystallinity is dependent on the crystallization mechanism. Although a well-developed phenomenological description of the crystallization pro-

cess exists, the molecular details still need to be unraveled. An understanding of the molecular basis of crystallization kinetics appears to be the key to the control of the macroscopic properties of semicrystalline polymers.

(36) E. Ergöz, J. G. Fatou, and L. Mandelkern, *Macromolecules*, **5**, 147 (1972).

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Applying Electron Spectroscopy for Chemical Analysis to Industrial Catalysis

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ESCA (electron spectroscopy for chemical analysis), also known as XPS (x-ray photoelectron spectroscopy), is rapidly emerging as an important industrial technique for studying a variety of surface phenomena including catalysis, corrosion, band structure of solids, adhesion, and surface contamination. Because of the broad chemical and economic significance of catalysis, ESCA is being extensively explored as a means of obtaining new insights into both catalytic properties and phenomena.

The information contained in an ESCA spectrum which makes it particularly suited for catalyst investigations is the determination of elemental surface composition, chemical bonding of surface atoms, and chemical and physical changes on the catalyst surface which may occur as a consequence of reaction. In this Account, the manner in which ESCA can be used to investigate catalytically important phenomena will be described. However, before proceeding with applications to specific catalyst systems, a brief review of some of the fundamental information inherent in an ESCA spectrum will be discussed. This will be followed by a general description of sample preparation and handling.

For a more detailed description of the fundamentals of ESCA, the reader is referred to the excellent books of Siegbahn et al.,^{1,2} as well as numerous review articles encompassing a wide variety of applications.³

Fundamentals of Electron Spectroscopy

In an ESCA experiment, the sample under high vacuum (10^{-8} – 10^{-10} Torr) is irradiated by a source of low-energy x rays, generally Al $K\alpha$ (1486.6 eV) or Mg

$K\alpha$ (1253.6 eV), and the kinetic energy of the ejected electrons is measured under conditions of high resolution and precision. A photoelectron spectrum is a plot of the number of electrons detected vs. their kinetic energy. The kinetic energy of a photoelectron depends on the energy of the exciting radiation and the energy with which the electron is bound to its nucleus. The core electrons are those which are generally monitored in an ESCA measurement. Even though they are not directly involved in chemical bonding, their energies are influenced by the chemistry involved in bond formation. The binding energy of the electrons is calculated from the energy of the exciting x radiation and the kinetic energy of the electrons which escape from the sample without significant energy loss using Einstein's photoelectric equation

$$E_{BE} = E_{x\text{ ray}} - E_{KE}$$

Although the x-ray photons penetrate deeply into the sample, the electrons which escape without energy loss come from the outermost surface layers since low-energy electrons have very short mean free paths in solids. It is estimated that these electron escape depths range from about 10 Å in metals to about 100 Å in organic polymers. Thus, the electrons detected in an ESCA experiment are representative of a very small amount of material, material which is present on the surface of the sample. Extreme care must

(1) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, J. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA; Atomic, Molecular and Solid State Structure by Means of Electron Spectroscopy", Almqvist and Wiksells, Uppsala, 1967.

(2) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.

(3) Only a few of the numerous review articles on applications of ESCA are cited here: (a) D. M. Hercules, *Anal. Chem.*, **42**, 20A (1970); (b) J. M. Hollander and W. L. Jolly, *Acc. Chem. Res.*, **3**, 193 (1970); (c) W. N. Delgass, T. R. Hughes, and C. S. Fadley, *Catal. Rev.*, **4**, 179 (1970); (d) W. E. Swartz, Jr., *Anal. Chem.*, **45**, 788A (1973); (e) W. Bremser, *Fortschr. Chem. Forsch.*, **36**, 1 (1972); (f) W. L. Jolly, *Coord. Chem. Rev.*, **13**, 47 (1974); (g) D. M. Hercules and J. C. Carver, *Anal. Chem.*, **46**, 133R (1974); (h) C. R. Brundle, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 291 (1974); (i) J. S. Brinen, *ibid.*, **5**, 377 (1974).

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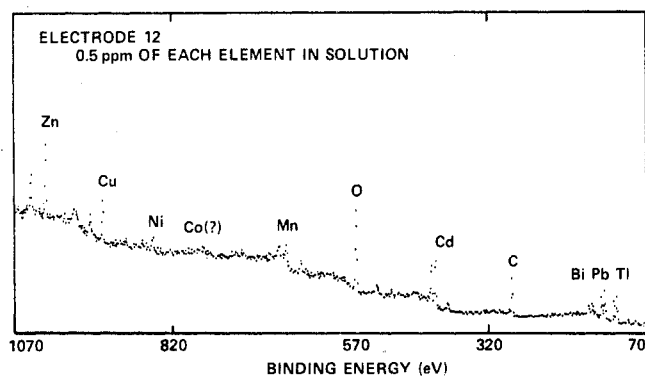


Figure 1. Survey scan of a glassy carbon electrode upon which nine metals, initially present at 0.5 ppm, have been electrodeposited.

therefore be taken in applying ESCA results to bulk properties of materials.

The binding energy of core electron lines from all the elements has been tabulated by Siegbahn et al.,¹ and the presence of an element in a material can be assigned by comparison with the observed electron lines. In general, this assignment can be made unequivocally since nearly all the elements have at least two electrons with binding energy lower than the x-ray energy. All the elements, except hydrogen, have been detected by ESCA. Figure 1 demonstrates both the surface sensitivity of ESCA and the ability to clearly distinguish the presence of various elements. The sample is an electrode prepared by depositing metal ions, present in solution at the 500-ppb level,³¹ on the surface of a glassy carbon electrode.⁴ The spectrum spans an energy region of 1000 eV and is commonly referred to as an elemental or survey scan. At these bulk levels the elements would not be detected by ESCA. Under optimum conditions, for an impurity with high cross section in a matrix of low cross section, detection limits approaching ~0.01% may be achieved.

Changes in the chemical bonding around an atom in a molecule produce shifts in binding energy which can readily be measured (1–10 eV), although they are generally small relative to the total kinetic energy. In some instances, these chemical shifts are due to differences in the "oxidation state" of the atom, and in other cases the formal "oxidation state" is unchanged and shifts arise from differences in chemical environment. It has been pointed out that detailed analysis of chemical shifts is a rather complex problem.^{5–7} In addition, other phenomena such as shake-up peaks, multiplet splittings, and satellite peaks can complicate the spectrum.^{8,9} Caution must therefore be exercised in ascribing additional peaks to new chemical species.

Figure 2 shows spectra of MoO₃ supported on alumina in the oxide form (fresh catalyst) and partially sulfided form (activated catalyst).³¹ This binding en-

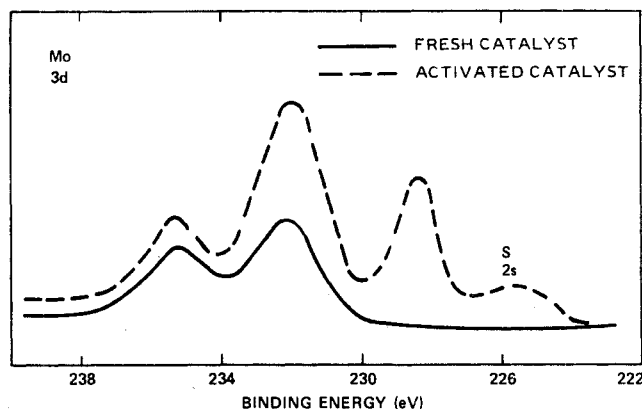


Figure 2. The Mo 3d spectrum observed from fresh (—) and activated (---) MoO₃ on Al₂O₃ catalysts. Note the presence of both the oxide and sulfide species in the spectrum of the activated catalyst.

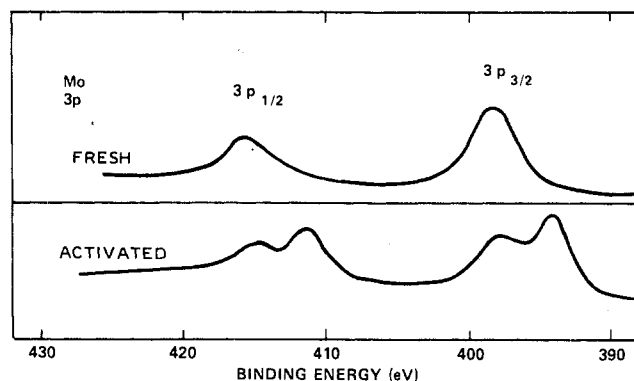


Figure 3. The Mo 3p spectrum observed from fresh (—) and activated (---) MoO₃ on Al₂O₃ catalysts. The presence and relative amounts of the two different types of Mo species present on the activated catalyst can be more readily seen due to the increased spin-orbit splitting of the 3p electrons.

ergy region shows the Mo 3d spin-orbit lines. Spin-orbit interaction results in the appearance of doublets, which are not always resolved, for electrons having non-zero orbital angular momentum (all except s electrons). Furthermore, the relative intensities of the spin-orbit pair are given by the ratio of multiplicities. Thus, for d electrons the intensity ratio is 6:4; for p electrons 4:2, and for f electrons 8:6. This fixed intensity ratio is particularly valuable in extracting chemical information from complex spectra. The spectrum of the activated catalyst shows the formation of another Mo species, chemically shifted by ~3 eV to lower binding energy, approximately the same energy as spin-orbit splitting. The complex nature of the used catalyst spectrum can then be interpreted in terms of the presence of two Mo species. From the intensity relationships, the relative amounts of oxidized and reduced Mo species present on the surface may be estimated. Figure 3 shows the Mo 3p lines for these same catalysts.³¹ Since the spin-orbit splitting increases in a given element as one moves to more tightly bound electrons, the existence of the two Mo species can be more readily recognized and relative abundances can be estimated more reliably.

To summarize, ESCA measurements can provide:

(1) qualitative elemental analysis of surfaces with sensitivity to all elements except hydrogen; (2) inherently high sensitivity to small amounts of material

(4) J. S. Brinen and J. E. McClure, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 243 (1974).

(5) H. Basch, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 463 (1974).

(6) D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 135 (1974); D. A. Shirley, *Chem. Phys. Lett.*, **16**, 200 (1972); **17**, 312 (1972); and D. W. Davis and D. A. Shirley, *ibid.*, **15**, 185 (1972).

(7) P. H. Citrin and D. R. Hamann, *Phys. Rev. B*, **10**, 4948 (1974).

(8) T. A. Carlson, J. C. Carver, L. J. Saethre, F. G. Santibanez, and G. A. Vernon, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 247 (1974).

(9) T. A. Carlson, J. C. Carver, and G. A. Vernon, *J. Chem. Phys.*, **62**, 932 (1975).

present on the surface;¹⁰ and (3) chemical structure information relating to oxidation state and charge distribution by observation of chemically induced shifts.

Sample Preparation and Treatment

Sample mounting techniques depend on the type of sample under investigation and to some degree on the nature of the spectrometer employed. Powdered samples generally allow for the greatest variety of mounting procedures. These include: (1) pellet formation—powdered samples may form pellets by themselves or may be pressed into an inert matrix such as graphite for spectral examination; (2) double-sided tape—the tape is mounted on a suitably flat metal platen and the powder is then dusted or gently pressed onto the sticky surface; (3) other tacky surfaces, such as conductive paint or soft polymers such as poly(methyl methacrylate), used to support powders; and (4) pressing powders into soft metals, etched aluminum, or wire mesh screens. Each of these methods has its particular merits and disadvantages. Pellet formation requires application of pressure which generates considerable heat that could produce changes in the surface composition of the sample. In general, this procedure is found to be quite satisfactory, particularly for experiments involving measurements at elevated temperature. Double-sided tape is useful for powders which do not form pellets or which cannot be pressed into graphite. Contamination of the surface by volatile constituents of the tape has been found to be insignificant. Pressing powders into wire mesh screens or scraping onto roughened surfaces is reported to provide satisfactory spectra, although these may be less homogeneous than the aforementioned.

Catalyst pellets can be mounted in depressions made in flat sample platens and held in place by tape or by forced fit if temperature studies are to be performed. Little difficulty is encountered in mounting metal films. In situ vapor deposition, evaporation from solution in an inert atmosphere in a drybox or N₂-filled glovebag attached to the spectrometer, cleaving, or abrading under vacuum are all methods which have been successfully employed to obtain spectral information on the bulk properties of materials.

The short escape depths of the electrons being monitored by ESCA means that surface impurities can dominate the spectrum unless some care is taken in sample preparation. Typical sample treatments employed are washing with an appropriate volatile solvent (which primarily removes carbon contaminants), abrading with ultrafine abrasive paper or diamond tool, and argon ion etching. The nature of the problem may preclude any or all of these treatments. Etching with argon ions cleans the surface of metal foils to remove all traces of carbon or oxygen, but can chemically change the surface of metal oxides or alloys. For industrial problems the nature of the impurity coating can be more significant than information regarding bulk chemistry.

(10) For example, the work of C. R. Brundle and M. W. Roberts, *Proc. R. Soc. London, Ser. A*, 331, 383 (1972), C. R. Brundle and M. W. Roberts, *Chem. Phys. Lett.*, 18, 380 (1973), and T. A. Mahey, J. T. Yates, and N. E. Erickson, *ibid.*, 19, 487 (1973), indicates a minimum detectability of ~10% of a monolayer.

Applications to Catalysis

While the exact binding energy contained in the spectrum provides specific information regarding chemical structure, this information is not always the most significant in catalyst studies. Differences in binding energies between treated or untreated catalysis and differences in relative intensities are often more informative. Subtle changes in chemical bonding, resulting either in a broadened spectrum or the appearance of shoulders on the peaks of spectra from the starting material, imply formation of new species which may be crucial in the understanding of catalytic activity. The kinds of information which can be obtained from ESCA measurements and which are of direct import to catalysis studies involve promoter distribution, dispersion studies, and surface conductivity as detected by charging effects. Examples of such studies are given below.

Promoter Distribution. One of the many factors contributing to catalyst performance is related to the distribution of promoter(s) on the support material. Surface chemical analysis by electron spectroscopy can provide a measure of the distribution by monitoring the relative intensities (areas) of promoter and support electron lines. Figure 4 shows an elemental scan for two catalyst extrudates, curves A and B. Curve B' was obtained from a ground sample of B and is intended to represent a measurement of the bulk properties. The relative intensities of Mo:Al, Co:Al, and P:Al are much higher in B than in A. Wet chemical analysis performed on the catalysts indicated that bulk concentrations were essentially identical. When the extrudates were ground, the ESCA spectra, curves A' (not shown) and B', were obtained and were essentially identical with each other as well as with A. The combination of these observations suggests the existence of promoter gradient in catalyst B even though they were fabricated by identical synthesis. Some variable in the synthesis of B obviously changed, leading to a catalyst with gross promoter inhomogeneities and an unacceptable catalyst.

A closer look in the 0–200-eV binding energy re-

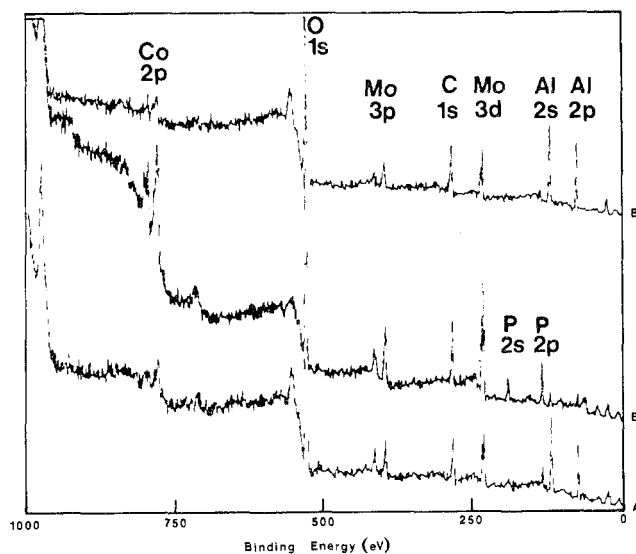


Figure 4. Survey scans for catalysts A and B covering the binding energy range of 0–1000 eV. B' is the spectrum obtained from a ground sample of B.

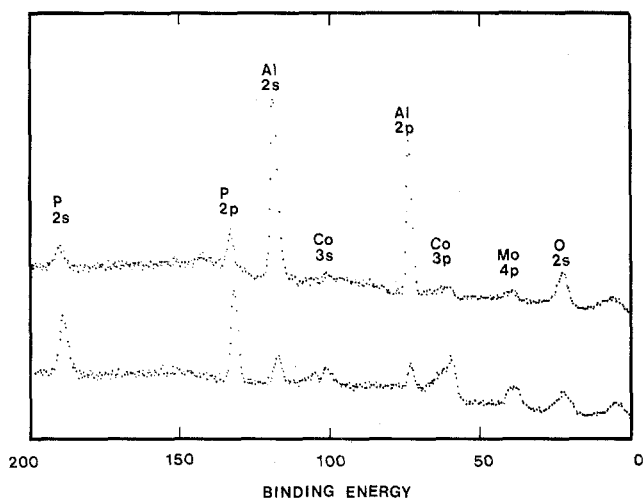


Figure 5. The 0–200-eV binding energy region for catalysts A and B shown in Figure 5. This region clearly points up the differences in the relative amounts of Mo, Co, and P on the Al_2O_3 surface.

Table I
Hydrogen Chemisorption Results

Catalyst loading ^a	Rh Dispersion ^b
A, 3.3%	0.10
B, 6.5%	0.12
C, 11.9%	0.12

^a Rh metal weight percent. ^b Defined as no. of surface Rh atoms/total no. of Rh atoms.

gion, Figure 5, points out more vividly the differences in the two catalysts. This region contains some of the weaker lines of Co and Mo as well as the Al and P lines. Quantitative analysis of solids by ESCA is complex because photoelectrons escape without loss of energy from only the outermost layers. Electrons of different kinetic energies may penetrate the sample to different extents.^{3c} It is therefore more exact for this type of comparison to use lines from the various elements which are close in binding energy. In this spectrum, Mo 4p, Co 3p or 3s, Al 2p or 2s, and P 2p lines are close enough to assure that the sampling depth is fairly constant. In practice, the use of weak lines (Mo 4p or Co 3p) is too time consuming, and the stronger lines are generally used, Co 2p and Mo 3d or 3p. It must be remembered that escape depth considerations are important factors for quantitative interpretation of spectra from heterogeneous samples. To obtain an estimate of the discrepancy incurred in using strong lines of widely different energies, relative intensities of weak to strong lines from homogeneous samples (foils or well-characterized compounds) can be determined and compared with heterogeneous samples (catalysts). However, caution must still be exercised since relative cross sections and electron attenuation lengths may not be identical for heterogeneous and homogeneous systems.

Dispersion. An example demonstrating the use of ESCA in obtaining both physical and chemical information on catalyst structure comes from our continuing study of Rh/C catalyst.¹¹ Conventional hydrogen chemisorption measurements performed on these implied that the dispersion of rhodium, defined as the

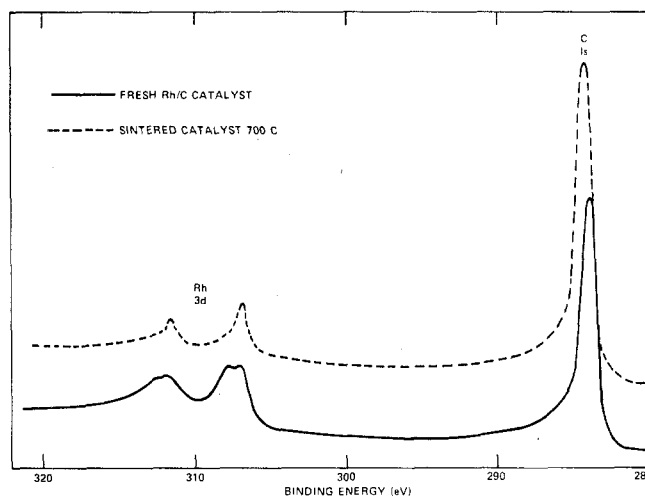


Figure 6. Spectra showing the results of heating the Rh/C catalyst in hydrogen at elevated temperature. The solid curve shows the C 1s and Rh 3d lines for the fresh catalyst while the dashed spectrum was obtained heating at 700 °C for 5 h.

ratio of the number of surface Rh atoms to the total number of Rh atoms, was independent of metal loading. Table I summarizes these results for three different catalyst loadings. The insensitivity of dispersion with respect to metal loading was unexpected and pointed to the possibility that physical changes were taking place on the surface during the chemisorption measurements. A combination of ESCA and XRD (x-ray diffraction) measurements was undertaken to investigate this point. The solid curve in Figure 6 shows both the C 1s and Rh 3d lines for the fresh catalyst, while the dashed curve shows the same spectrum obtained after heating this catalyst at 700 °C in H_2 for 5 h. The oxide species has disappeared as a result of the heat treatment in H_2 . A comparison of the Rh/C intensity ratio, determined from the areas under the C 1s and Rh 3d doublet using 20-eV sweeps before and after heating, shows a decrease by a factor of 2 caused by the heat treatment. Intermediate heating in H_2 at 400 °C, the temperature employed for pretreatment in the chemisorption measurements, for 15 min shows an intermediate decrease in the Rh/C intensity ratio.

The Rh/C intensity ratio determined from ESCA measurements can be used to monitor the relative amounts of surface rhodium accessible for ESCA detection and is related to the dispersion on the charcoal support. Scharpen, for example, has used (Pt/Si) ESCA ratios, as a function of Pt loading to monitor dispersion.¹² In the ESCA experiments on rhodium described here, the metal loading is kept constant at 12%.

XRD patterns on the three catalysts discussed above showed no discernible rhodium pattern for the fresh catalyst, implying that either very finely dispersed or amorphous rhodium was present. Crystallite growth is observed for the heated catalysts; the more vigorous the conditions the larger the crystallites. A plot of the ESCA vs. the XRD data is given in Figure 7.

These results show that reduction in H_2 at elevated temperatures affects the catalyst in two ways. The

(11) J. S. Brinen, J. L. Schmitt, W. R. Doughman, P. J. Achorn, L. A. Siegel, and W. N. Delgass, *J. Catal.*, in press.

(12) L. H. Scharpen, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 369 (1974).

Table II
Spectroscopic and Activity Results for Starting and Reduced Catalysts^a

	(Rh/C) Intensity	Crystallite size, Å	% relative conversion	K_w
Fresh catalyst	0.99	< 40	100	16
H ₂ , 75 °C, 30 min	0.82 (in situ)			
H ₂ , 400 °C, 15 min	0.76	75	35	4
H ₂ , 700 °C, 5 h	0.47	235	< 1	< 0.1
He, 400 °C, 15 min	0.85	77		
He, 700 °C 2 h	0.64	100		

^a ~12% rhodium on charcoal.

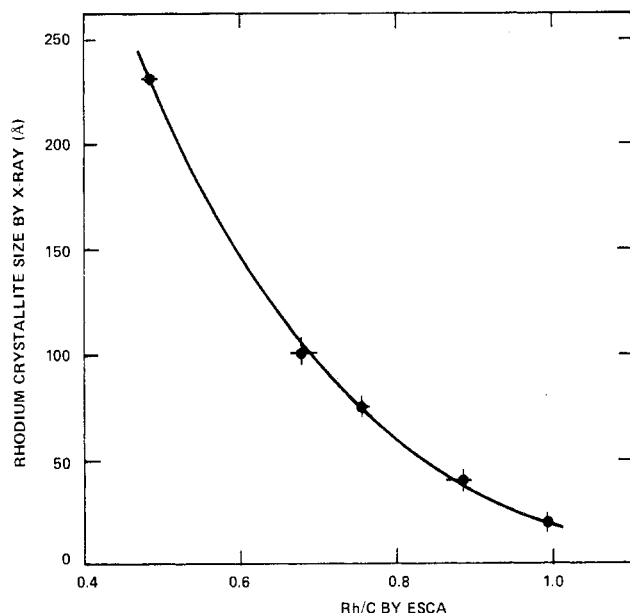
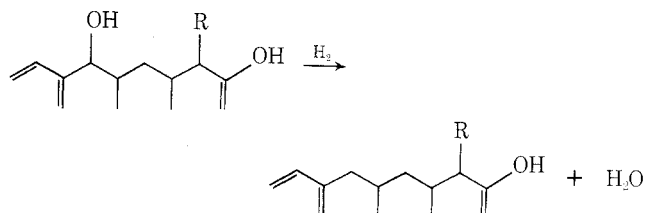


Figure 7. A plot showing the Rh/C intensity ratio obtained from ESCA measurements vs. the Rh crystallite size determined from x-ray diffraction measurements.

most obvious is that the surface oxide component undergoes reduction to the metal. Valence band spectra, Figure 8, of Rh foil and fresh catalyst reduced in the spectrometer sample treatment chamber to eliminate potential reaction with the environment are virtually identical and are substantially different from the fresh catalyst. As a result or in conjunction with this reduction, the rhodium atoms tend to "flow", resulting in the formation of larger clusters of metal. Thus, the independence with respect to metal loading of the rhodium dispersion measured by H₂ chemisorption is due to sintering produced by heating at elevated temperatures.

The physical and chemical changes should be reflected in the performance of the catalyst. To test this, the rate of disappearance of the reactant and the first-order rate constant, K_w , were obtained for the test reaction:



The results, tabulated in Table II, together with ESCA and XRD data, show the dramatic decrease in catalyst performance as a result of the sintering process.

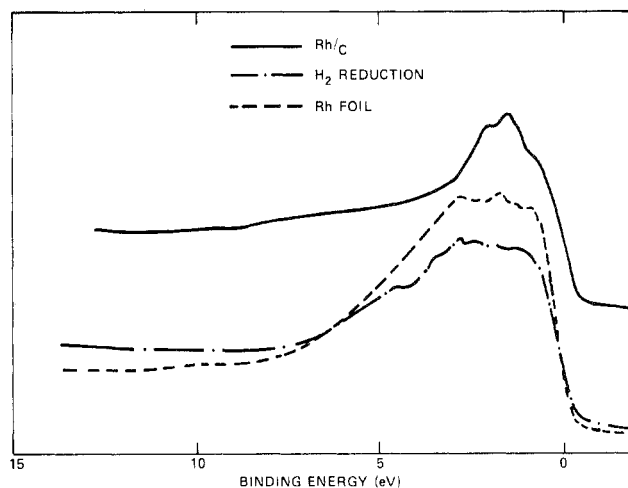


Figure 8. A comparison of the valence band spectra of Rh foil, a fresh Rh/C catalyst, and an in situ reduced Rh/C catalyst.

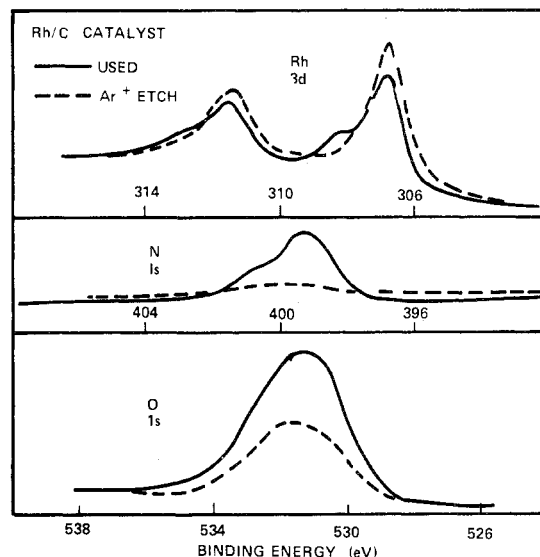


Figure 9. Spectra obtained from a used Rh/C catalyst before (—) and after (---) mild etching with argon ions.

Catalyst activity generally decreases as a function of time, and can even become zero after extended use. Although bulk chemical analyses may show no appreciable loss in promoter level, the deterioration may be attributable to physical and chemical changes as discussed above. Another mode of deterioration involves the deposition of reactants or reaction products onto the catalyst surface which tends to coat the catalytically active sites. As an example, Figure 9 shows Rh 3d, N 1s, and O 1s lines from a used catalyst which is no longer highly active. Note the build-up of N and O from the reaction mixture. Mild Ar ion etching demonstrates the surface nature of this coat-

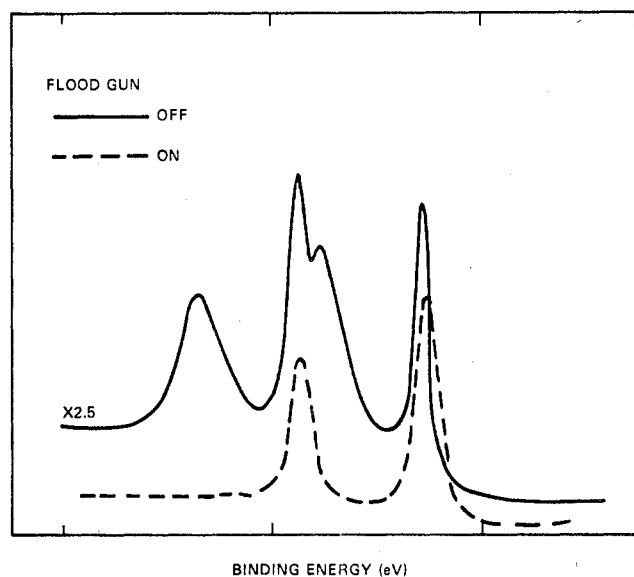


Figure 10. Spectra illustrating the presence of conducting and insulating domains on the surface of an industrial catalyst. The insulating domains are sharpened and are shifted to lower binding energy when the flood gun is applied.

ing. Nearly all the N is stripped off the catalyst surface. Ar ion etching also results in chemically reducing the surface Rh species.

Charging Effects. A major problem in interpreting ESCA spectra of solids, particularly semiconductors or insulators, is the effect known as charging. Sample charging occurs as a consequence of the photoelectron process. Electrons ejected from the sample create a positive surface charge when they are not compensated for by the other electrons present in the sample. For insulators or semiconductors this compensation does not readily occur and an equilibrium potential is established at the surface. The distribution of surface charge is broad and ill defined, and the escaping electrons are affected by this additional "potential drag". Electron lines from insulating samples are generally broad and appear at higher binding energies than expected. Spectrometers using monochromatic x radiation for excitation tend to exaggerate charging because the Brehmstrahlung radiation, which can create a source of secondary electrons from the window separating the excitation and analyzing compartments, is prevented from impinging onto the sample surface. Shifts due to charging can be as large as chemical shifts or even larger, and can be confused with shifts due to changes in chemistry.

There are at present two manifestations of charging: the usual charging which results in shifting and broadening all of the electron lines in the observed spectrum, and differential charging in which only some of the lines in the spectrum are affected. Figure 10 shows an example of the latter effect. Although the supported catalyst is proprietary, the principle exemplified by the spectrum is sufficiently important to be included in this Account. The solid line shows a spectrum which consists of four lines, two sharp and two broadened, which could easily be attributed to two oxidation states from the same element (two sets of spin-orbit doublets). Our Hewlett-Packard spectrometer is equipped with an electron flood gun. This enables the surface of the sample to be flooded by a

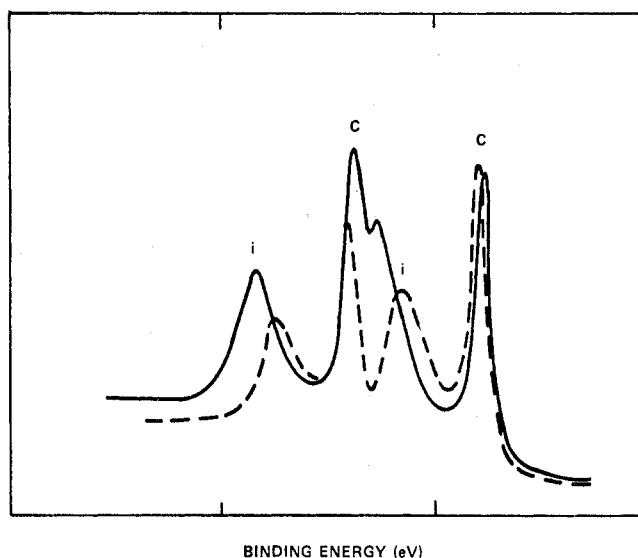


Figure 11. Spectra of two catalysts with slightly different activities which differ in the relative abundance of insulating regions on the catalyst surface.

source of nearly monoenergetic electrons which can be varied between 0 and 10 eV. Charging effects can thus be monitored by application of the external source of electrons and compensating for the buildup of surface charge in insulating materials. When the flood gun is turned on, the dashed curve in Figure 10 is obtained. The broad pair of lines have sharpened and shifted to lower binding energy so that they are at exactly the same binding energy as the lines from the conducting domain. This is evidenced by the intensity increase in these lines. When voltage is applied to these electrons, the lines from the insulating species would reach a constant line width, but would continue to shift to lower binding energy with increasing voltage. Lines from the species in the conducting domains would not shift at all.

For spectrometers which do not employ monochromatic radiation for exciting photoelectrons, the effects of charging are much less severe and complications in spectral interpretation are considerably diminished. However, as will be shown below, differential charging can provide valuable information regarding the surface conductivity of catalysts and can be used without complete knowledge of the physics and chemistry involved. For these spectrometers, differential charging can be observed by application of a potential to the sample holder. Lines from species which are in good electrical contact with the sample are not affected by the applied voltage, while those not in electrical contact do shift with the applied voltage.

A difference of a few percent in the activity of a catalyst may often mean the difference between a commercially viable or unprofitable process. Figure 11 shows the spectra for two catalysts (similar to those just discussed which differ slightly in activity). The primary difference between the two catalysts, after scrutiny by a variety of techniques, was seen in their respective ESCA spectra—namely the relative abundance of insulating domains. These spectra were obtained from retained samples of commercial catalysts, i.e., unused. The ESCA data provide a criterion for predicting, prior to use, whether the catalytic ac-

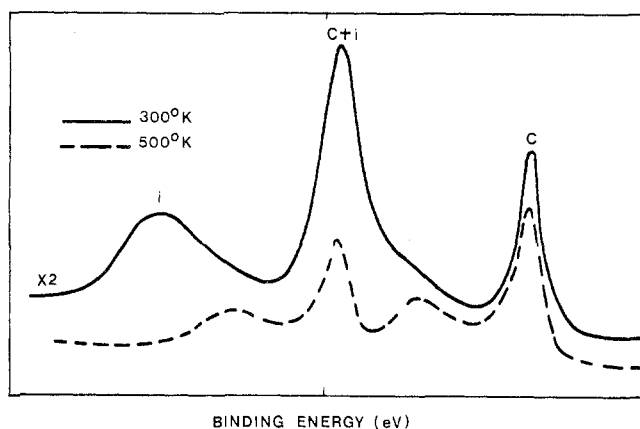


Figure 12. Spectra showing the result of elevated temperature on the insulating domains on a catalyst surface.

tivity will be acceptable, and such results have been used for this purpose.

It has been pointed out that sample charging could be affected by factors such as temperature and hydration^{3c} which may alter the conductivity of the surface. An example of temperature effects on differential charging is shown in Figure 12. As the temperature is increased the surface insulating domains decrease and the lines associated with these domains shift to lower binding energy and decrease in intensity. Cooling the heated catalyst back to ambient temperature results in a reversible change back to the starting spectrum. In addition to demonstrating the temperature behavior of surface conductivity, this spectrum clearly demonstrates that the spectrum of the catalyst at room temperature bears little resemblance to that of the catalyst at or near the temperature of reaction. In favorable cases, chemical and electrical differences observed at elevated temperatures can aid in the elucidation of catalytically important chemistry.

Directions of ESCA in Catalysis

It is evident by now that ESCA can provide valuable information concerning the nature of chemical surfaces involved in catalytic processes. In order to be increasingly more valuable, laboratory experi-

ments should, whenever possible, simulate actual process conditions. For example, if elevated temperatures are involved, spectra should be obtained as close to the operating temperature as possible. Although spectra cannot as yet be obtained under actual operating conditions, reactions can be performed in sample treatment chambers on the spectrometer so that the activated or used catalyst need not be exposed to air and possible unwanted chemistry prior to spectroscopic examination. We have performed catalyst activation and actual catalytic processes in the spectrometer sample treatment chamber, and spectra were obtained without exposure to the atmosphere. The addition of a small quadrupole mass spectrometer in the reaction chamber to monitor the chemical process could be extremely valuable in establishing correlations of activity with ESCA observables. Other surface monitoring techniques such as Auger, LEED (low-energy electron diffraction), SIMS (secondary ion mass spectrometry), etc. can be integrated with an ESCA spectrometer to provide a much clearer picture of the chemical surface of catalysts.

Angular dependence studies of flat surfaces¹³ can enhance the surface sensitivity and further distinguish between bulk and surface properties. This technique is particularly informative for flat surfaces such as oxide coatings on metal foils or contaminants on polymer surfaces. The extension of these measurements to less regular surfaces, like those of catalysts, has not been fully explored. It is possible that this type of measurement could be used to monitor promoter distributions in even thinner layers than conventional ESCA measurements.

As was discussed in the text, charging effects complicate the ESCA spectra of catalysts supported on insulators such as silica and alumina. A clearer understanding of charging leading to reliable binding energy information of insulating materials is greatly needed for characterization of chemical species on catalytic surfaces.

(13) W. A. Fraser, J. V. Florio, W. N. Delgass, and W. D. Robertson, *Surf. Sci.*, **36**, 661 (1973); C. S. Fadley, R. J. Baird, W. Siekhaus, T. Novakov, and S. A. L. Bergstrom, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 93 (1974).