ADVANCES IN CATALYSIS

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Preface

In our present volume Bart completes his review of X-ray absorption methods, in a chapter with Vlaic dealing with EXAFS, or extended X-ray absorption fine structure. This method, with its ability to provide structural information on active sites in amorphous catalysts under working reactor conditions, is clearly of great potential importance. The second article, by Driscoll, Campbell, and Lunsford, describes the investigation of radical desorption into the gas phase and its implications for catalytic mechanisms, and a process probably underlying catalytic ignition, a problem going back to Davy and Döbereiner. Iwasawa's article deals with the preparation and characterization of metal atom ensembles by reacting metal carbonyls or other complexes with oxide surfaces. Apart from their interest to industry, these new surfaces are helping to advance our knowledge of kinetic mechanisms. EXAFS is involved in this work also.

van Santen and Kuipers in their article bring information on recent single crystal surface science studies to elucidate the mechanism of ethylene oxide formation on silver catalysts, and their conclusion that adsorbed oxygen atoms rather than molecules are involved marks a return to the idea of G. Twigg. Our last two articles serve to remind us of the continuing power of traditional organic chemical methods in catalysis. Pines shows us how preparative conditions by modifying NiO content, and hence acidity, can change the character of nickel catalysts, with similar modification arising from sulfidation. Mąkosza and Fedoryński review the phenomenon of phase transfer catalysis, in which typically a lipophilic cation ferries a reactive anion across the interface from an aqueous medium to a reactant molecule dissolved in an organic solvent. Surely there is an interesting parallel to be drawn between this latter process and the active transport and ion pumps operative in certain biological membranes.

DANIEL D. ELEY

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Extended X-Ray Absorption Fine Structure Studies in Catalysis

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I. Introductory Statement

A. OBJECTIVES

The principal theme of this contribution is concerned with the application of X-ray absorption spectroscopy (XAS) [primarily various forms of extended X-ray absorption fine structure (EXAFS) studies] to the study of problems in catalysis.

Knowledge of the identities and spatial arrangement of the atoms composing a catalyst (and especially its surface) is fundamental for the understanding of the material's properties. In the case of solids with long-range order this information is usually obtained by X-ray or particle beam diffraction techniques. For materials without long-range order this procedure is less useful and electron microscopy is virtually the only tool from which structural parameters are inferred in a direct fashion. Spectroscopic techniques, such as electron spin resonance (287) and Mössbauer (122) and photoelectron spectroscopy (21, 395), offer insight into other aspects of the structure but often only indirectly.

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In recent years considerable progress has been made in the understanding of catalytic phenomena through a multitechnique approach of characterization of catalysts. This approach is justified if one considers the formidable problems to be overcome in catalysis in order to arrive at an understanding of the bulk and surface structure, electronic properties, and atomic composition, all of which are necessary ingredients in relation to the chemical reactivity of the solid. Several of the techniques impose severe constraints on the experimentalist [e.g., ultrahigh-vacuum (UHV) conditions and single-crystal samples in low-energy electron diffraction (LEED) (313, 322)], which therefore distract the attention from the actual conditions of the catalytic process. In this respect high-voltage electron microscopy (HVEM) and X-ray absorption and Mössbauer spectroscopy are exemplary in that they allow *in situ* studies of actual catalyst samples. Although electron *emission* spectroscopies, in particular X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), have acted as primary tools in applied catalysis during the 1970–1980 decade, X-ray absorption analysis methods are now rapidly assuming growing importance. This is immediately obvious from the rapid growth in published papers (Fig. 1) and the number of reviews dealing with various aspects and applications of XAS to catalysis (23a, 102, 169, 175a, 213, 215, 216, 242, 262, 262a, 272, 297, 363, 403, 434, 496, 500, 501b).

The delay in takeoff of XAS as compared to XPS, techniques which both use X-ray excitation, is undoubtedly connected with differences in photon source intensity (intense characteristic radiation in XPS experiments, weak broadband radiation in XAS). The revival of X-ray absorption spectroscopic techniques, in particular EXAFS, overcomes many of the limitations of other physicochemical techniques.

X-Ray absorption spectroscopy is essentially an old tool for the investigation of electronic structure and local environment of specific atoms in matter. The potential impact of XAS on catalysis has long been recognized (351) and it is
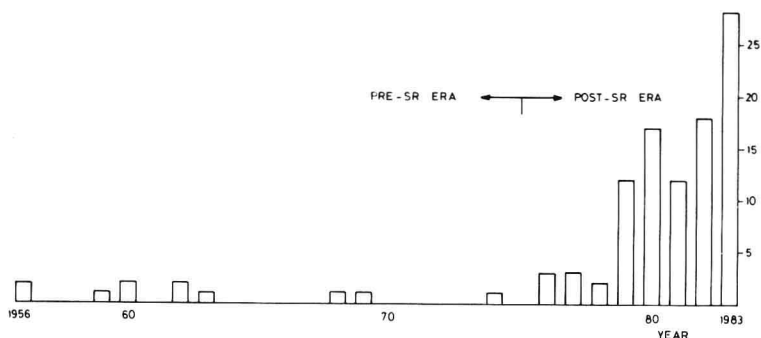

Fig. 1. Growth of the literature (number of papers) on X-ray absorption spectroscopy in catalysis from 1956 to 1983.

not surprising that this branch of science was one of the areas of application of EXAFS specifically encouraged by Lytle in an exposition (288) marking a renewal of interest in the technique. Based upon this encouragement and with the benefit of subsequent developments in physics, namely the advent of high-flux synchrotron radiation (SR) sources, which have opened up a wide range of the electromagnetic spectrum and have essentially removed the practical limitations due to the low intensity of the older photon sources, rapid progress was made in EXAFS-catalyst studies, both basic and applied, starting with the period 1975–1980. Although in some cases immaturity of the technique produced insignificant contributions, sufficient success was achieved to catalyze a more productive period (1980–present) characterized by more rigorous data collection and data analysis procedures. This second phase was further greatly stimulated by the important advancements made in the underlying theory during the first period.

The extent of information obtainable from XAS data varies from a simple confirmation that a given chemical element is present in the sample to a unique description of the short-range order together with details concerning the electronic structure of the system (bulk, surface, or adatoms). Of particular importance to the catalytic chemist is the fact that electronic and structural information is obtained simultaneously and that this branch of spectroscopy offers unique possibilities for studying bulk samples and surface species, ordered and disordered systems, and high and low concentrations of active sites in both *ex situ* and *in situ* conditions. Furthermore, the technique is ideally suited for studies of small-particle systems, and in several instances information about morphology can also be obtained.

In this paper, various chemical phenomena that are pertinent to catalysis and can be studied through XAS will be discussed. The information gained comprises atom–atom distances in the first several coordination shells surrounding the absorber, coordination numbers, the charge on the absorbing atom, the state of the outer electrons of the absorber, and the nature of the interactions between the catalytic material and support and between catalyst and gases (chemi- or physisorption). To date the greatest efforts have been made with XAS applied to metal catalysts, but aspects relating to metal oxides and sulfides have also been considered. The modification of surfaces during chemisorption, surface segregation, and catalytic reactivity are other important topics.

The physical basis of XAS and the experimental procedures will first be introduced to the nonspecialist. A broad coverage of the past and present involvement is given by an extensive survey of the literature and the developments are illustrated on the basis of an appreciation of the powers and limits of the various (sub)techniques and by a comprehensive series of examples. To minimize the size of the text, practical details have almost completely been ignored, and for such information the citations should be

consulted. Nevertheless, problems involved in analysis of EXAFS data and those peculiar to characterization of catalysts using SR photon sources are indicated. No claim is made to the effect that the review is exhaustive, but every effort has been made to include work through the end of 1983. In selected cases more recent references are cited.

B. DEVELOPMENT OF X-RAY ABSORPTION SPECTROSCOPY

The first X-ray absorption spectrum was observed by de Broglie (*109*) and the fine structure near inner-shell absorption thresholds was detected as early as 1920 by Fricke (*143*), Hertz (*186a*), and Lindh (*282*). Near-edge structures were originally interpreted by Kossel (*245*) in terms of assignment to excited electronic states. Subsequently the extended structure beyond 20 eV from the edge (now called EXAFS) was observed (*231, 386*), for which Lindsay (*283*) and Coster *et al.* (*100*) advanced an interpretation on the (erroneous) basis of simultaneous transitions of two or more electrons after absorption of an X-ray quantum. In 1931 Kronig (*255*) developed a long-range order (LRO) theory for solids, now known to be incorrect, depending on Bragg scattering of the ejected photoelectrons by the extended lattice array, which accounted for many experimentally observed features (similar structure for similar lattices, inverse R^2 dependence, correct R versus T dependence, and increasing energy separation of the fine structure features with energy from the edge), but failed to account for others. Further developments by Kronig (*256*) and Peterson (*367*) led to a short-range order (SRO) theory for molecules in terms of backscattering of a photoelectron by neighboring atoms with the recognition of the concept of phase shifts in the photoelectron wave function (*367*) due to the central and backscattering atoms. The basic understanding of the problem was due to Kostarev (*246*) and further developments by Kozlenkov (*248*) resulted in a simplified version of the modern theory of fine structure with neglect of the mean free path and disorder effects. The original theory was further implemented stepwise by the introduction of the mean free path as a measure of the lifetime of the excited photoelectron and core hole state (*408*) and by the Debye–Waller-type factor to account for thermal disorder due to lattice vibrations (*420*). This finally resulted in the first bond distance determinations from XAS spectra by Levy (*276*) and Lytle (*288, 289*). Chemical information using near-edge structure was also obtained by Mitchell and Beeman (*330*) and Van Nordstrand (*351*). A further landmark in the application of XAS consisted in the measurement of the first X-ray spectra (Al K edge) from the Frascati synchrotron by Cauchois *et al.* (*76*) in 1963, but it took another decade before regular use was made of such a facility for the purpose of routine X-ray absorption spectroscopy in transmission mode (*232*)

or for recording X-ray spectra during a catalytic reaction (356). Meanwhile, Lytle (288) had devised an empirical short-range order theory for solids, which reduced the problem to resonances within the first coordination sphere. In spite of these developments, discussions and confusion about the SRO and LRO theories continued until quite recently (14, 15, 365). Rapid theoretical progress was made in particular through the pioneering contributions of Lytle, Sayers, and Stern (410, 411, 443, 449), who derived a theoretical expression for the undulations beyond 50 eV from the threshold, which became known as "extended X-ray absorption fine structure." They showed that a single-scattering SRO theory adequately explains these structures and derived a Fourier transform theory for EXAFS which has great potential for the determination of local structures around selected absorbers. Other important contributions came from Ashley and Doniach (12) (adaptation of LEED theory to spherical geometry), Lee and Pendry (273) (treatment of multiple-scattering effects), and Teo and Lee (466) (amplitude and phase functions).

The interested reader is referred to Refs. 13, 267, 294, 361, and 424 for further details on the historical developments of X-ray absorption spectroscopy.

C. EXAFS CATALYST STUDIES: PAST AND PRESENT

Until the advent of SR sources and advancements in the theoretical understanding of the extended X-ray absorption fine structural features, little or no use was made of the technique in catalysis studies. On the contrary, the experimentally more pronounced but theoretically more difficult to interpret edge features have more frequently been measured for systems of catalytic interest (23a, 29, 36, 177, 178, 226–228, 277–280, 351, 404, 514).

The important advancement in contemporary studies compared to those undertaken more than a decade ago is that experimental methods have emerged which enable rapid probing and that theoretical progress has allowed suitable data analysis procedures to be devised. At the same time it is noticed that whereas EXAFS has for long been cultivated mainly by physicists, its potentiality is now fully exploited by catalytic chemists.

Synchrotron radiation research has recently been treated comprehensively by Winick and Doniach (510), Koch et al. (239), and others (189, 257, 258, 344) for all the major applications in the X-ray and ultraviolet part of the spectrum. Topics such as EXAFS and its use in the study of condensed materials, with applications to catalysis, biology, and materials science, have been discussed. At the same time other aspects of the rapidly expanding field of EXAFS and X-ray absorption near-edge structure (XANES) spectroscopy, ranging from understanding the underlying physics to data analysis procedures, have been covered by Teo and Joy (465), as also illustrated by a variety of applications.

The field of X-ray spectroscopy using SR is now expanding rapidly into a variety of different research areas and EXAFS and XANES have become truly interdisciplinary methods for use in many branches of science (*35*). X-Ray beam lines are now designed specifically for X-ray absorption studies (*409*). A comparison of various SR sources is given by Thompson *et al.* (*468*).

X-Ray absorption spectroscopy conferences are being scheduled biannually (*35*) and books dealing with the topic have appeared (*2, 13, 41, 374, 465*). General descriptions of basic principles and applications (*44b, 61, 196, 243, 272, 294, 357, 378, 447, 463, 533a*) and more specialized reviews dealing with a variety of subjects [crystalline materials (*236*), amorphous solids, liquids and solutions (*172, 180, 194, 264, 286, 403, 418a*), glasses (*163, 379a, 398a*), disordered materials (*180, 311*), dilute systems (*179, 312*), metallurgy and metallic glasses (*106, 169, 180, 516*), superionic conductors (*54, 55*), organometallic compounds (*80*), biological and bioinorganic chemistry (*104, 119, 298, 423*), biophysics (*44a*), ionic polymers (*208, 358, 525*), materials science (*169, 273a, 516b*), energy-related matters (*516a*), bimetallic clusters (*434*), metal clusters (*368a*), small particles (*133a*), and various other aspects of catalysis] have been published. The present article was designed both to be instructional and to review the rapidly expanding catalytic literature. The more general aspects of the XAS technique are presented strictly from a functional viewpoint and the choice of the catalytic subject matter was judged in relation to its utility and degree of effort produced by the academic and industrial community.

II. Description of Experimental Requirements

As may be seen from Fig. 2, which shows the arrangement of XAS experiments in transmission mode, an X-ray absorption setup consists of three primary components: (1) a source of X-rays, (2) a monochromator (and collimator), and (3) a detector.

Broadband radiation is processed by a monochromator which passes an almost monochromatic (i.e., $\sim$ 1-eV spread) beam onto the sample. The actual energy selected can be varied by rotating the channel-cut (or double) crystal
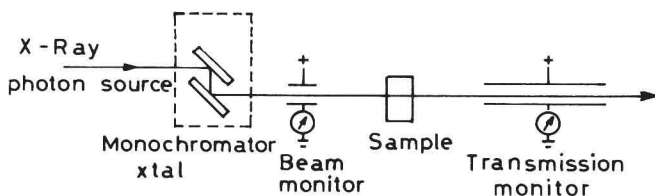
FIG. 2.   Schematic diagram of X-ray absorption measurements by transmission.

monochromator. A basic XAS experiment therefore involves measurement of the total linear absorption coefficient μ (cm^{-1}), which is a function of the wavelength and the nature of the absorber, as the photon energy is varied across and beyond the absorption edge. In case of a transmission experiment we write Beer's law:

$$I(E) = I_0(E) \exp[-\mu(E)x] \tag{1}$$

where I_0 and I are the photon intensities before and after passage of the beam through the absorber of thickness x, as measured by ion chambers in the X-ray beam path. The illuminated area of a sample is about 15×3 mm for most SR sources.

A. SAMPLE PREPARATION

For examination of X-ray absorption fine structure, data acquisition is greatly facilitated by using specimens with a relatively high attenuation (typically 70–90%) of I_0 at the wavelength just above the appropriate absorption edge. The optimal signal/noise (S/N) ratio for transmission experiments occurs at a thickness of the sample (in any aggregation state), regulated by $\mu x \approx 1$–2. The signal intensity can be improved at low temperature by attenuation of the Debye–Waller factor. In practice the sample thickness varies from several micrometers for pure metals to some millimeters for dilute samples. Compilations of X-ray cross sections in the 1-keV to 1-MeV range as a function of the nature of the absorber are given in Refs. 77, 199, and 323.

Reproducible production of solid specimens with the desired absorbance properties is required. Eanes et al. (123) describe a technique for the preparation of stable and uniform solid specimens suitable for X-ray absorption studies in the range of thicknesses useful for EXAFS and XANES examination. Sample homogeneity (to be controlled under the optical microscope) is critical for transmission experiments. Concentrated materials with high absorption coefficients may be diluted with low-Z inert materials (usually BN). For dilute samples ($\sim 10^{-3}$ M) it may be necessary to use the fluorescence technique.

Samples are usually prepared as self-supporting wafers by pressing the well-ground catalyst powder or alternatively by sandwiching a thin, uniform layer of particulate material between thin plastic films in a rigid frame (123). The mass M (grams) of material needed to form a specimen with the desired absorption characteristics is given by:

$$M = A \ln (I_0/I) \bigg/ \sum_i f_i (\mu/\rho)_i \ln(I_0/I) \tag{2}$$

where $A =$ the area (centimeters) of the sample target, f_i is the weight fraction

of the *i*th element in the sample, and $(\mu/\rho)_i$ is the mass absorption coefficient for the *i*th element at the wavelength of interest.

At low energies, absorptions due to the sample cells and intervening gases can pose problems. The former difficulty can be reduced by use of X-ray transparent windows, the latter by use of a helium path.

B. PHOTON SOURCES

The experimental setup requires a broadband photon source, either Bremsstrahlung produced by a conventional or rotating anode, or alternatively synchrotron radiation from a storage ring or a laser X-ray source. Poor experimental conditions have long been a deterrent for the application of this branch of spectroscopy, known to X-ray physicists already for over 50 years.

Studies of the extended X-ray absorption spectrum using conventional sealed X-ray sources and single flat-crystal monochromators require several weeks of data collection to achieve satisfactory statistics (see e.g., refs. *289* and *293*). The reason is that the fine structures of interest represent only a few percent or less of the absorption coefficient $\mu(E)$. For reliable measurements neither random nor systematic errors should exceed 0.1% of $\mu(E)$, and with a dilute sample even higher accuracy is required.

The main present sources of continuous X-radiation used for XAS studies are synchrotron radiation—emitted by relativistic electrons (or positrons) at the bending sections of storage rings—or Bremsstrahlung, from a rotating anode X-ray tube. Various reviews describe and compare X-ray photon sources (*42, 58, 124, 171, 239, 254, 270, 300, 508*), X-ray detectors (*219, 268, 471*), and monochromators (*43, 320*). In particular, very broadband, highly collimated, intense photon beams from high-energy electron storage rings (Fig. 3) have recently revolutionized the applications of photon absorption spectroscopy in the hard (4–30 keV) and soft-to-intermediate (0.8–8 keV) X-ray energy regimes. Synchrotron radiation stations are now increasingly becoming available where it is possible to perform transmission and fluorescence experiments with low- and high-temperature sample treatment capabilities and a UHV chamber for surface studies. Consequently, SR is now most commonly used as the best and most versatile photon source. Precisely pulsed SR X-ray sources, with fluxes of 10^8–10^{10} photons s^{-1} per eV bandpass at about 10 keV, improve the brightness by 10^5–10^6 over that obtainable from conventional sources. This allows scan times for EXAFS data collection of about 20–30 min. Among the desirable properties of SR (*124, 239, 257–260, 441, 508*), we further mention:

1. Qualitatively known characteristics.
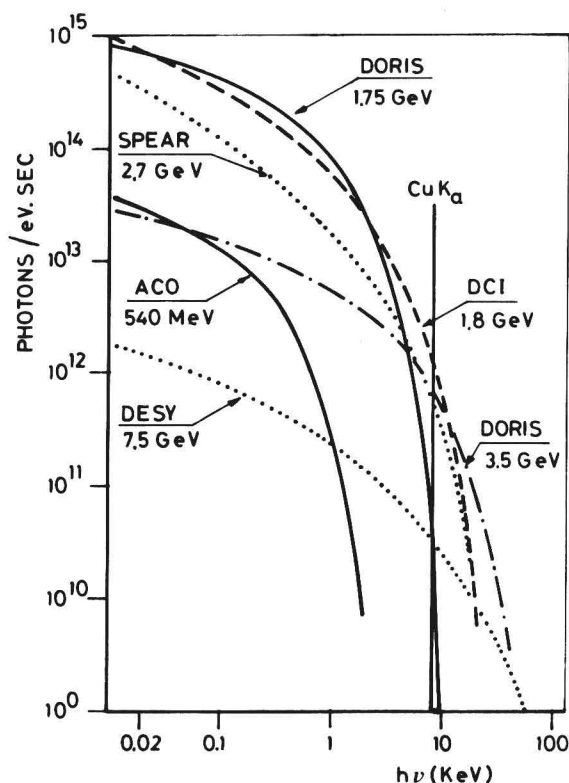2. Wide spectral range (spanning the gap between the infrared and X-ray range).

FIG. 3.   Spectral distribution of synchrotron radiation from various sources.

3.   High spectral brilliance (10^3 times over characteristic lines of conventional X-ray tubes) decaying with a half-life of several hours and with fluctuations well under one part in 10^3.

4.   Tunability over a wide energy range (3–25 keV) with a continuous spectrum (up to a cutoff in the soft or hard X-ray region, determined by the electron energy and orbit radius).

5.   High collimation (emission angle of radiation is smaller than 0.1 mrad).

6.   Well-defined polarization (almost perfect in the orbital plane of the electron beam (319)), useful for single-crystal and surface studies.

7.   Pulsed time structure (nanosecond pulses separated by microsecond to millisecond intervals), useful for time-dependent studies (329a).

Further increases in flux and extensions of the available energy range are prospected with the combined use of focusing mirrors and wiggler magnets