

# Spectroscopy in Heterogeneous Catalysis

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# SPECTROSCOPY IN HETEROGENEOUS CATALYSIS

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## PREFACE

The expanding role of spectroscopy in both the science of catalysis and the practical utilization of heterogeneous catalysts has created a need for a book which will serve as an introduction to the most widely employed types of spectroscopy in the field. The aim of this book is to fill that need by providing a basis on which researchers and potential researchers in heterogeneous catalysis can evaluate and initiate spectroscopic experiments. Our intent has been to include in each section an overview of the concepts and capabilities of a particular technique, enough theory and detail on experimental procedures to help those seriously preparing to take measurements, and examples of all proven or potentially important applications. Attention has been paid to the use of spectroscopic measurements in guiding empirical approaches to applied problems as well as to fundamental studies of the chemical identity of catalytic surfaces.

We assume that both industrial and academic readers will have a strong interest in catalysis, but not necessarily a background in a particular type of spectroscopy. The book has been used as a text for courses at the graduate level and is intended as a practical introduction for those who are active in industrial research and development.

In the introductory chapter we stress the interrelation of the techniques and the advantages to be gained by an approach which incorporates several spectroscopic as well as kinetic measurements. Responsibility for preparation of the succeeding chapters has been divided among the authors: IR and Raman (Haller), diffuse reflectance and photoacoustics

(Kellerman), Mössbauer and XPS (Delgass), and ESR and NMR (Lunsford). We have aimed, however, at a unified presentation.

The leader of this venture has been Lunsford. We are indebted to many colleagues and students for critical reading of the manuscript. We acknowledge, particularly, E. Holstein-Delgass for assistance in preparing the index.

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## *Chapter 1*

# INTRODUCTION

### 1.1 The Scope of Spectroscopy in Catalysis

The development of catalysts is a complex process in which many factors contribute, including basic science, intuition, screening programs, and engineering. Catalyst technology and science have progressed simultaneously and in a complementary manner. For example, technological advances in the utilization of supported bimetallic clusters have greatly stimulated basic research on alloys and multimetallic systems. Similarly, one may anticipate that a more complete understanding of the structural and mechanistic details of a catalyzed reaction will lead both directly and indirectly to the development of new and better catalysts.

The most sensitive probe of a catalyst's performance will continue to be the rate and selectivity of a chemical reaction. While these macroscopic observations are adequate for determination of how good a catalyst is, such a kinetic analysis requires supplementary microscopic information to remove ambiguity in the deduction of the reaction mechanism. It is for this microscopic information concerning the nature of active sites, the structure and reactivity of intermediates, and the identification of poisons that one turns to spectroscopic methods.

Catalysis is by definition a kinetic process, and therefore it might be expected that spectroscopy in heterogeneous catalytic research would provide

information on reaction intermediates obtained under steady state or dynamic reaction conditions. The paucity of papers in which reactive intermediates have been unambiguously identified testifies to the difficulties involved in attaining this goal. Nevertheless, it is important to realize that other types of spectroscopic experiments can still advance catalytic research. More generally we study the adsorbed phase in equilibrium with the gas phase, which is relevant to catalysis if the adsorbed species probes the structure of the site to which it bonds, or can be expected or shown to be reactive when a second reactant is added, temperature is increased, pressure is changed, etc. Frequently, the stable adsorbed species giving rise to the spectrum coexists with the reactive intermediate which is too low in surface concentration to be observed. Even in this case, the experiment is still relevant to catalysis because it provides information about the structure and composition of the surface of the working catalyst. Thus, investigation of adsorption (physical, chemical, reversible, irreversible, etc.) by spectroscopic techniques will always contribute to our understanding and is a necessary part of the science of catalysis.

Before considering the details of the individual spectroscopies, we will try to place each area of investigation into the full spectrum of catalytic research and also to relate the various spectroscopic approaches to each other. Many important general features of the field of catalysis emerge from the simple schematic of a catalytic reactor in Fig. 1-1. A catalyst is a substance which, though not itself consumed, provides a new reaction pathway with a lower activation free energy and therefore a faster reaction rate to the desired products. Both historically and logically the first question to ask is: "What is the new pathway?" The answer is normally sought by modeling the reactor as a transfer function between reactants and products, which is the chemical kinetic approach. Ambiguities of classical steady state analysis of products as a function of reactants can be resolved through isotope tracer work and unsteady state reaction analysis, but even in the most favorable cases structural

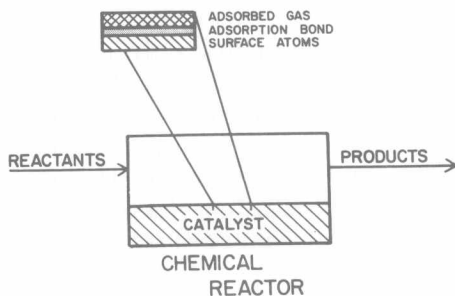


Fig. 1-1 Schematic representation of the gas-solid interface.

information on surface intermediates and the nature of the active site cannot be obtained. Furthermore, kinetic data alone leaves completely unanswered the question: "Why did the reaction pathway change?"

A solid catalyst can provide a new reaction path only by direct contact with the reacting gases. Thus, our attention focuses immediately on the gas-solid interface, without which there would be no heterogeneous catalysis. Although physical characterization of solid surfaces, particularly measurement of surface areas, is well developed, it is in the area of chemical characterization of catalysts and the gas-solid interface that spectroscopy has and will continue to have its greatest impact in heterogeneous catalysis.

Catalyst characterization takes many forms with each being related differently to the primary object, the chemistry of the interface. Bulk characterization of solids is a well developed experimental science and provides a starting point for understanding the chemistry of catalysts. While it is true that the surface is built on the underlying bulk, the surface chemistry is not easily extracted from, or uniquely determined by, the bulk properties. This puts a premium on direct observation of the surface, including its stoichiometry, structure, electronic properties, and chemical characteristics. Thus, of the various available tools, those which have surface specificity are likely to be most important.

There is also a hierarchy in the nature of the application of spectroscopic techniques. Analysis of a catalyst before it is put in the reactor, even under optimum conditions, describes the surface chemistry of the precursor to the working catalyst. This information is more directly related to the questions at hand than is the characterization of the bulk, but even the stoichiometry of the solid surface can change in response to changes in the gas phase. This observation emphasizes the need for *in situ* surface characterization, during adsorption, or better still, during reaction. In the context of Fig. 1-1, we would like to look inside the reactor at the gas-solid interface. An expanded view of the interface shows three regions of interest: the solid surface, the adsorbed molecules, and the true interface, the gas-solid bond. In order to study these regions on an atomic scale, we must observe the interaction of radiation from various portions of the electromagnetic spectrum with the interface, i.e., we must carry out spectroscopic experiments. Even with this information in hand one must establish whether or not the observed chemistry is the *catalytically important* chemistry. To answer the question, knowledge of the interface must be coupled with knowledge of the molecular steps and the rate of reaction. The most successful method to date accomplishes this by perturbing the reaction system by a sudden change in reactant concentration, isotopic mixture, temperature, etc., and comparing the dynamic response of the interface and the reaction. Kinetically important surface species are differentiated by relaxation times which correspond to the requirements of the kinetic

analysis. It is important to recognize that a key requirement for reaching this goal is sufficient sensitivity of the spectroscopy for the active species.

The answers to the fundamental questions provided by the approach outlined above will form a basis for expansion of catalysis as a predictive science. However, the more fundamental approach represents only a narrow segment of catalytic research and development. For a real chemical reactor we must be concerned with the time evolution of catalyst behavior caused by nonidealities such as impurities, upsets in operating conditions, side reactions, and changes in the catalyst itself. Furthermore, the need to solve problems and develop new processes in a limited time requires that decisions often be based on the best information available, and not necessarily on complete understanding. The urgency of applied research also puts high priority on information directly related to the seat of catalytic activity, the interface. The advantages that make spectroscopy important to fundamental research can also serve applied research and development. Correlation parameters such as the IR frequency of adsorbed gases or the relative intensities of x-ray photoelectron peaks can guide an experimental program by indicating when catalysts are different and suggesting empirical routes to catalyst optimization. Particular advantages of each technique for applied research will be discussed, when appropriate, in the following chapters.

The ideal spectroscopy for catalytic applications would provide for identification of adsorbed species, as well as information on the intramolecular and intermolecular bonding in adsorbed molecules and surface atoms, the motion of adsorbed molecules, and the symmetry and oxidation state of surface atoms. Moreover, it should be possible to obtain the spectrum over a wide range of temperature and pressure without interference from the gas or bulk catalyst phases. Although this ideal spectroscopy does not exist, a judicious use of the several spectroscopies to be discussed in the following chapters can provide much of the desired information.

The applicability and limitations of the individual spectroscopies are summarized in Table 1-1. The first column indicates the type of quantum transition involved for each particular spectroscopy. In most cases the measured parameter is the energy associated with a transition between two levels of the same kind, i.e., vibration, electron spin, nuclear, etc.; this energy range is indicated in the second column. Photoelectron spectroscopy is an exception to the above generalization since the transition is from an electronic level of an atom to an unbound state, i.e., an ejection of an electron. It also differs from the other spectroscopies in the relation between the radiation used and the mode of detection. That is, in all of the other spectroscopies considered the absorption, emission, or scattering of radiation as a function of energy (wavelength) is monitored, while in photoelectron spectroscopy it is the kinetic energy of the electrons ejected by the radiation (x ray) that is measured.

TABLE 1-1 Comparison of Several Types of Spectroscopy

Spectroscopy	Transition energy (eV) <sup>a</sup>	Kind of transition	Sample size or form	Applicable range of			Information primarily on	
				Pressure (atm)	Temp. (°C)	Solid surface	Molecule to surface bond	Adsorbed molecule structure
Infrared	$(50-2.5) \times 10^{-2}$	Vibrational	10-100 mg pressed wafer	0-1	<200		X	X
Raman	$(50-0.6) \times 10^{-2}$ <sup>b</sup>	Vibrational	100 mg powder	0-1	<1000			X
Visible/near infrared	0.5-6.5	Electronic, vibrational	1-1000 mg powder	0-1	<300	X	X	X
Mössbauer	$10^4-10^5$	Nuclear	50-500 mg	$0-2 \times 10^5$	<1500 <sup>c</sup>	X <sup>d</sup>		
ESR	$(14-3.8) \times 10^{-5}$	Electron spin	100-500 mg powder	0-10	<300 <sup>e</sup>	X	X	X
NMR	$(2.5-8.3) \times 10^{-7}$	Nuclear spin	1-5 g powder	0-5	<400	X	X	X
X-ray photoelectron	0.1-1500	Bound electron to the continuum	$\sim 0.1 \text{ cm}^2$ of surface	$0-10^{-4}$	<2500	X	X <sup>f</sup>	X

<sup>a</sup>  $1 \text{ eV} = 8065.7 \text{ cm}^{-1} = 2.418 \text{ Hz}$ .<sup>b</sup> The energy range of the incident and scattered radiation is  $\sim 2 \text{ eV}$ .<sup>c</sup> Depends on isotope and sample.<sup>d</sup> Detects all Mössbauer atoms in sample; therefore, high surface sensitivity requires concentration of Mössbauer atoms at the surface.<sup>e</sup> Upper temperature limit strongly influenced by the relaxation time of the paramagnetic species.<sup>f</sup> This bond is seen better in ultraviolet photoemission.

The full range of temperature and pressure over which catalysts operate is rarely practical for any one spectroscopy (see columns four and five). The pressure range is often limited by absorption by the gas phase of the photons or electrons to be detected. This is a particularly severe problem for photoelectron spectroscopy because the electron mean free path is small even at modest pressures. In the case of Mössbauer spectroscopy the nuclear transitions are associated with the catalyst and not the gas phase. Because of this fact and the penetrating ability of gamma radiation, a pressure limitation is almost nonexistent for Mössbauer spectroscopy. Most of the spectroscopies have upper temperature limits due to level population or relaxation effects. The limitation is greatest for those spectroscopies where thermal energy can be large compared to the transition energy between levels, i.e., NMR and ESR. The problem can be circumvented, in principle, for infrared (Raman) by measuring emission (anti-Stokes Raman lines) rather than absorption (Stokes Raman lines) at higher temperatures where the excited vibrational levels become populated. The nuclear transitions of Mössbauer spectroscopy are clearly too great to be affected by thermal effects, but there still exists a temperature limit due to lowering of the recoil-free fraction. Observation of the extremely small natural linewidths of gamma-ray fluorescence (Mössbauer spectroscopy) requires that the recoiling (fluorescing) atom be anchored to the remainder of the solid to minimize recoil energy dissipation. At higher temperatures the higher mean square displacement of the Mössbauer atom in the solid decreases the probability of recoil-free absorption.

For all spectroscopies there exist restrictions on the size, form, and nature of the sample to be studied. Fundamental restrictions such as the requirement for unpaired electrons in ESR spectroscopy, or one of a small number of Mössbauer-effect nuclei, necessarily limit the kinds of adsorbents or catalysts to which these spectroscopies can be applied. This is not as restrictive as it may at first seem because molecules or atoms which have the required properties may be used as probes. For example, the nature of adsorption sites on a wide variety of catalysts may be probed by measuring the ESR spectrum of adsorbed NO. Moreover, iron, a very good Mössbauer atom, may be ion exchanged into oxide surfaces or alloyed with metal catalysts and used to probe local surface chemistry around it.

Typically, samples for all spectroscopies considered may be studied in the form of a powder or pressed pellet which is very similar to practical catalysts, but care must be taken to adjust particle size and pellet thickness to avoid excess scattering and absorption, respectively. For very penetrating radiation such as used in Mössbauer spectroscopy, it is also important to support the absorbing atoms to attain a high surface to volume ratio since Mössbauer nuclei in the bulk will be detected but will not provide information concerning the surface. Photoelectron spectroscopy presents just the opposite problem.

The fact that the ejected electrons can only penetrate 10–100 Å of solid makes the technique very surface sensitive, but may also mean that only the superficial surface of a very porous catalyst can be analyzed while the major portion of the catalytic action occurs within the pores.

The applicability of each spectroscopy will be treated in the individual chapters, but some comments on the last column of Table 1-1 are appropriate. With ingenuity and careful selection of the systems to be studied, it is probably possible to apply all spectroscopies to all three regions of the interface shown in Fig. 1-1. But, there are one or more portions of the interface where each spectroscopy finds general and natural application. Infrared, Raman, and ESR spectroscopies have been primarily used to determine structure and bonding within the adsorbed molecule and to a lesser extent the bond to the surface. From changes in the structure and bonding observed when adsorption occurs, deductions about the adsorption site can often be made. Optical, Mössbauer, and x-ray photoelectron spectroscopies provide more direct information on the composition of the surface and the structure of the adsorption sites. NMR spectroscopy has generally been used to study molecular motion at the surface and, less frequently, to investigate the bond between adsorbed molecules and the surface.

Infrared has as its primary advantage a wide applicability to nearly any dispersed metal or oxide catalyst. The information provided by a vibrational spectrum is so fundamental to molecular structure that many books on infrared are entitled "molecular structure." The same kind of structural information comes from Raman spectroscopy, but for many catalysts different selection rules make it possible to extend the frequency range relative to that which is accessible by infrared spectroscopy. This capability, however, is offset by a considerable loss in sensitivity. Optical (uv-vis) spectroscopy may be used to determine the local symmetry and oxidation state of a transition metal, thus it is a sensitive probe for the type of site in which that ion exists. The applicability of optical spectroscopy however is not restricted to transition-metal containing systems, but may be extended to measuring the electronic spectrum of adsorbed molecules. Perturbations in the electronic structure of adsorbed molecules are the rule rather than the exception and only optical spectroscopy gives direct information about their excited, as well as the ground electronic states. ESR is perhaps the most sensitive of all the spectroscopies to be discussed. The simple confirmation of the existence of a paramagnetic ion or atom for a given catalyst-adsorbent system constitutes important structural information, but under favorable conditions it is also possible to determine electronic and geometric structure, symmetry, and reactivity of adsorbed atoms and molecules. The primary application of NMR spectroscopy to surfaces has not been structural; it is used to follow relaxation phenomena from which it is possible to deduce molecular motion and

magnetic interactions at the surface. The strong point of Mössbauer spectroscopy is its adaptability to *in situ* experiments and its sensitivity to the chemical environment of the Mössbauer atom. Oxidation state, coordination number and symmetry, and alloy formation, particle size, etc., may be determined but detailed interpretation is often complex. Photoelectron spectroscopy has breadth as its greatest strength. It is applicable to any element but hydrogen in or on the surface and provides information on both the amount and chemical state of each component in the surface. While the subtleties of quantitative analysis of porous materials and interpretation of chemical bonding are still topics of research, much useful chemical information is revealed by photoelectron spectroscopy.

The above list is not intended to be exhaustive but illustrative of the importance and the particular merits of each spectroscopy for the study of catalysts. This is perhaps accomplished in a more effective manner by concrete examples of applications, as is done in the following paragraphs.

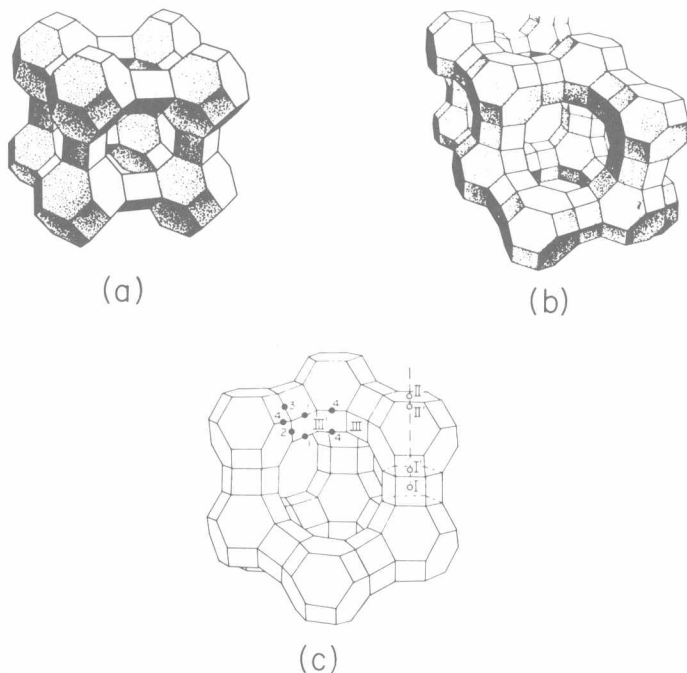
## 1.2 Applications of Spectroscopy to Zeolite Catalysts

In order to illustrate the importance of spectroscopy in catalysis, we shall consider the information which has been derived from the application of six types of spectroscopy to one class of catalysts—zeolites. The industrial usage of these open-structured crystalline aluminosilicates has been one of the most significant developments in the history of catalysis. Today virtually every catalytic cracking operation employs zeolites. The rapid commercial acceptance of these materials has been paralleled by an intense effort to understand the many facets of their remarkable behavior. A sample of the catalytic chemistry of zeolites is provided in an excellent review by Venuto and Landis [1]. More general information on zeolites may be found in the proceedings of three International Conferences on Molecular Sieve Zeolites [2a–c], as well as in the recent book by Breck [3].

### A. Elucidation of Structure

Since structure frequently plays an important role in the catalytic activity and selectivity of zeolites, it is essential that one be able to determine the structure of new zeolites, as well as to detect changes in structure during the synthesis and use of the material. The structure of a given class of zeolites is usually based upon x-ray diffraction data which has been collected, when possible, on single crystals. In Fig. 1-2 are line drawings of two types of zeolite, type A and the mineral faujasite of which zeolite X and Y are sub-classifications. Although diffraction techniques have yielded a wealth of





**Fig. 1-2** Line drawings of zeolite structures: (a) type-A zeolite, (b) faujasite (X and Y), (c) faujasite showing cation sites (Roman numerals) and different oxygen ions (Arabic numerals).

structural information which could not have been obtained otherwise, one would desire supplementary information for new zeolites and a more routine approach to structural analysis. Flanigen *et al.* [4] have demonstrated that the infrared spectrum in the region of  $200\text{--}1300\text{ cm}^{-1}$  is a sensitive tool for indicating structural features of zeolite frameworks.

The infrared spectra of three zeolites and hydroxy sodalite are depicted in Fig. 1-3, and the zeolite infrared assignments are given in Table 1-2. It is apparent from the spectra that some of the bands shift in frequency when one aluminosilicate is compared with another, whereas others are almost structure insensitive. The basic building blocks in the zeolites are silicon-oxygen and aluminum-oxygen tetrahedra, both of which are referred to as  $\text{TO}_4$  tetrahedra. Flanigen *et al.* proposed that external tetrahedral vibrations, such as those in the double rings and the pore openings, are structure sensitive (as indicated by the dotted lines in Fig. 1-3), whereas other internal tetrahedral vibrations are not (as indicated by the solid lines). For example, the bands between  $500$  and  $600\text{ cm}^{-1}$ , attributed to the double ring structure, are absent in sodalite where no double rings exist. The positions of the infrared