



Springer

# Handbook of

# Advanced Catalyst Characterization

Wachs  
Bañares  
Editors

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Editors

# Springer Handbook of Advanced Catalyst Characterization

With 747 Figures and 45 Tables

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ISSN 2522-8692

ISSN 2522-8706 (electronic)

Springer Handbooks

ISBN 978-3-031-07124-9

ISBN 978-3-031-07125-6 (eBook)

<https://doi.org/10.1007/978-3-031-07125-6>

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## Preface

This Springer Handbook focuses on *Advanced Catalyst Characterization* and covers the cutting-edge catalyst characterization methods for heterogeneous catalysts in powder form. Special emphasis is given to characterization under relevant reaction conditions (in situ and *operando* spectroscopy) and catalysis dynamics. Each modern catalyst characterization method is covered by a leading expert that is intimately familiar with the specific method. Additionally, case studies are provided to showcase how the specific advanced characterization methods are now incorporated in the investigation of different types of heterogeneous catalytic materials in powder form.

The chapters are arranged in eight parts:

- Part I: Vibrational Spectroscopy
- Part II: Electron and Photoelectron Spectroscopy
- Part III: Electron Microscopy
- Part IV: Particle Scattering
- Part V: X-Ray Methods
- Part VI: Magnetic Resonances
- Part VII: Transient and Thermal Methods
- Part VIII: Soft Operando

This handbook brings the knowledge of leading experts and practitioners of characterization techniques for heterogeneous catalytic materials at the atomic and molecular levels, with emphasis on techniques that can operate under reaction conditions, thus providing an advanced characterization, closer to actual working conditions. The chapters in this handbook provide insights on emerging methodologies and advanced in situ and *operando* spectroscopy characterization methods for the characterization of the bulk and surface of solid catalytic materials. The application of in situ and *operando* spectroscopy to catalysis studies is poised to advance catalysis science by establishing fundamental structure-activity relationships that can potentially guide the molecular design of advanced catalysts.

We would like to especially thank the contributing authors since without their excellent contributions this handbook would not be possible.

Madrid, Spain, and Bethlehem, PA  
May 2023

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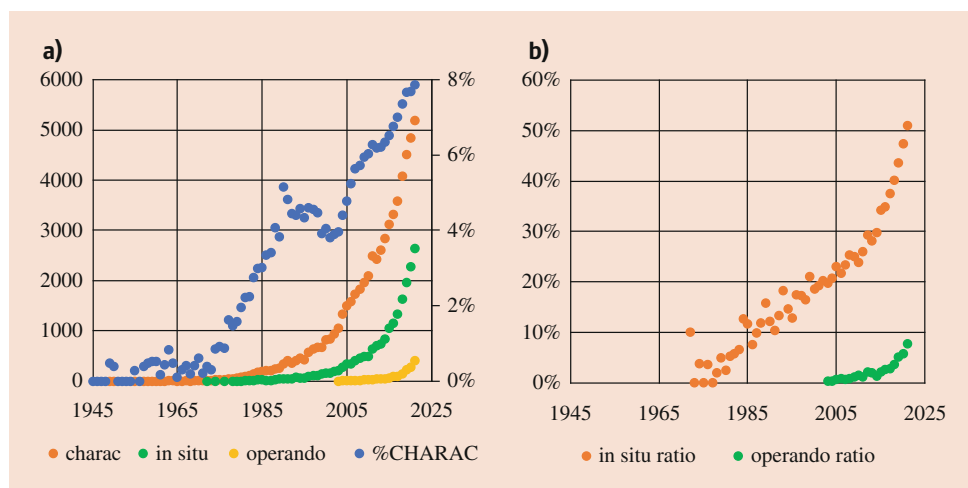
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## Editors' Introduction

*“in the beginning, . . . there was light . . .”*  
when light met matter, . . . there was spectroscopy.

**Catalysis** is a phenomenon that was initially not understood as first described by Berzelius in 1835 (*“I shall . . . call [the catalytic] bodies [i.e., substances] the **catalytic force** and the decomposition of [other] bodies by this force **catalysis** . . .”*) [1]. (After reviewing Eilhard Mitscherlich’s research on the formation of ether, Berzelius coins the word *katalys* (catalysis) on p. 245.) The nature of this **catalytic force** was not at all understood and required about a century for its understanding to begin since methods were not available to determine the state of the catalysts (surface and bulk) and the nature of the “catalytic force” and activated molecules (“[other] bodies”) during catalysis. Without knowledge of the catalyst structure and chemical state and their effects on reacting molecules, the catalyst was viewed as a black box and the fundamentals of catalysis couldn’t be established. In subsequent years, methods were developed based on the interaction of multiple radiation energies with matter that provided information about catalyst structure, chemical state, and activated molecules, which is the basis for *spectroscopy*. Illuminated by radiation, spectroscopy allows us to finally “see” the catalyst structures and chemical states (surface and bulk), catalytic force (active sites), activated molecules (reaction intermediates), and their dynamics as a function of environmental conditions and reaction time. In practice, *it is difficult to understand catalysis without spectroscopy, especially at the molecular level*.

The initial spectroscopic catalyst characterization studies appeared in the literature approximately in 1950, and the total number of reported catalyst characterization studies increased exponentially with time reflecting the desire of catalysis researchers to better understand how their catalysts function. The fraction of catalysis papers using “characterization” is constantly increasing over the years (Fig. 1a). Today, most of the heterogeneous catalyst publications include characterization studies. Of the reported characterization studies for heterogeneous catalysis, more than 50% use in situ methodologies and nearly 10% use *operando* methodologies (Fig. 1b). A few years after the early characterization studies were reported, in situ catalyst characterization studies began to appear. The term *in situ* is Latin and means “on site” and is used to refer to catalyst characterization studies under controlled environmental conditions (e.g., ultrahigh vacuum, reducing, oxidizing, dehydrated, molecular adsorption or reaction). Although the number of in situ catalyst characterization studies lags those of all catalyst characterization publications, more than 50% of all current catalyst characterization publications have incorporated in situ studies (Fig. 1b). The in situ characterization studies revealed that heterogeneous catalysts, especially the surface phases, are dynamic with respect to reaction environments and reaction time. This realization has recently prompted simultaneous catalyst characterization and performance measurements under reaction conditions. Such catalyst characterization studies are termed *operando*, from the Latin meaning “operating” [2, 3]. Having both catalyst characterization and performance data at the same time allows for directly establishing structure-performance relationships from the same location and at the same time, which minimizes variability when compared to independent measurements of structure and performance in different instruments and possibly reaction conditions. Although the term



**Fig. 1** (a) Number of papers with the term catalyst and “characterization” (orange); among these, those using “in situ” (green); and among those, those using *operando* (yellow); right axis, percentage of catalysis papers in all catalysis fields using the term “characterization.” (b) Percentage of papers using the term “in situ” in papers using “catalyst” and “characterization” (orange) and using the term *operando* in papers using “catalyst” and “characterization” (green). (Source: Scopus (July 9, 2022))

*operando* was just introduced into the catalysis literature in 2003, the number of *operando* studies has increased exponentially with time and now represents 10% of total characterization studies (Fig. 1b). The importance of in situ and *operando* characterization studies in heterogeneous catalysis research is reflected by the fact that they now account for ~60% of all catalyst characterization studies, and such studies will only increase with time.

We would like to point out that the term *in operando* has crept into the heterogeneous catalysis literature by analogy with the Latin term “in situ,” but this is an incorrect Latin expression. *In operando* means “on working (conditions),” which assumes that the catalyst is working, but since the catalyst is already working, the addition of the term “in” is incorrect. *Operando* is the correct term to use when performing simultaneous characterization and performance measurements of working catalysts.

### Analysis of Application of Characterization Techniques in the Heterogeneous Catalysis Literature

Catalysts are dynamic materials that can change with environmental conditions (temperature, pressure, gas/liquid composition, and reaction time). It is, thus, critical that the environmental conditions employed for measurements be specified to avoid confusion between the different states of the catalysts. Unfortunately, many literature studies can be found that do not indicate the measurement conditions. This is problematic since surfaces are usually hydrated and oxidized under ambient conditions and change upon heating in different environments. Under ambient conditions, the surfaces are solvated and not representative of the state of the surface under reaction conditions where solvation may be absent and the surface is populated by adsorbed reactants, reaction intermediates, and products. Furthermore, the incident radiation can also cause changes in the catalysts under certain conditions and corrupt the data. To avoid such confusion, the section below will examine the influence of environmental conditions and radiation sources on the state of the catalysts. Another confusion that exists in the catalysis literature is the assignments of the collected spectral information. Where possible, references will be provided that will assist in the spectral assignments and, thus, lead to reliable catalyst structure-activity/selectivity relationships.



### **Infrared (IR) and Sum-Frequency Generation (SFG) Spectroscopies**

Infrared spectroscopy (IR) provides the vibrations of the catalyst skeletal region and is primarily employed for examination of surfaces of solid catalysts to obtain molecular level information about surface hydroxyls, surface M=O bonds, adsorbed molecules, and reaction intermediates. As indicated above, the surface functionalities monitored by IR are strongly dependent on the environmental conditions. Experimental conditions do have an effect on the samples that infrared spectroscopy readily detects. Infrared can clearly identify the nature of surface species formed during reactions and it will deliver relevant information if the experiments properly reflect relevant reaction conditions. During in situ and *operando* IR spectroscopy studies under reaction conditions, it is important to distinguish between the vibrations of both adsorbed species and gas phase molecules because IR can give rise to strong vibrations of gas phase molecules. This is a great challenge, and several techniques may help discriminate between the gaseous and adsorbed molecules. For instance, reflection absorption infrared spectroscopy (RAIRS) can probe the structure and surface chemistry on model catalysts, taking advantage that only the polarization component of IR light that is parallel to the plane of incidence interacts with the molecules on the surface. These aspects and more are covered in the chapters by Busca, Negri et al., and Trenani and Ranjan. Furthermore, modulation-excitation spectroscopy methodologies, as described in the chapters by Urakawa et al., Ferri et al., and Collins et al., can be applied with polarized excitation to discriminate between gaseous and adsorbed species and their transient states during reaction. A step forward to investigate vibrational spectra of molecules located at surfaces and interfaces is infrared-visible sum frequency generation (SFG), described in the chapter by Pramhaas and Rupprechter, which is a nonlinear optical method that can identify such molecular structures with sub-picosecond time resolution and is applicable at nearly any interface that is optically accessible.

### **Raman Spectroscopy**

Raman spectroscopy is a very versatile optical spectroscopy to understand the working catalyst structure and surface chemistry in heterogeneous catalysis. Its extreme experimental versatility teams up with a growing number of instruments that continuously increases the characterization information. Raman experiments can be carried out under wide reaction conditions without any limitations of the sample phase. Raman is not only sensitive to crystalline phases, but it is a molecular spectroscopy with sensitivity to detect vibrations from amorphous surface metal oxide sites on oxide supports and small crystalline nanoparticles (<3 nm) that are difficult to detect with conventional XRD. These capabilities allow Raman to simultaneously provide information about both surface and bulk structures. The chapters by Moon et al. and Tigriripalli et al. describe the *operando* Raman advances in catalysis. Thus, it is critical that the experimental conditions be carefully provided (ambient, dehydrated, or reaction conditions). On rare occasions, the state of the catalyst can be affected by the laser irradiation (e.g., SiO<sub>2</sub>-based catalysts tend to dehydrate or the reducible metal oxide (e.g., CrO<sub>x</sub>) may reduce). This is especially a concern with deep UV Raman spectroscopy measurements that require using a fluidized bed to minimize exposure of the catalyst to the highly energetic UV laser (e.g., 244 nm) [4, 5]. UV-Raman spectroscopy may in turn provide powerful insight by a knowledgeable use of resonance-enhanced Raman scattering. Resonance-enhanced Raman can detect catalytic active sites that are in very low concentrations. UV Raman spectroscopy can also avoid fluorescence interference that hampers other visible-Raman measurements. Time resolution is still a challenge for *operando* Raman experiments; several approaches allow circumventing this limitation, signal enhancement by surface-enhanced Raman spectroscopy (SERS); near-field or modulation experiments are the way forward and are commented upon in

the chapter by Alvarez-Puebla. Engaging *operando* Raman and imaging in surface-enhanced Raman or tip-enhanced Raman spectroscopy (TERS) can increase time and space resolution that is presented in the chapter by Deckert-Gaudig et al. Furthermore, probing species at aqueous-solid interfaces, for example, we also include electrochemical reactions as a particularly exciting field for *operando* Raman, given the emerging relevance of electrocatalytic processes as commented upon in the chapter by Schuhmann et al.

### Ultraviolet-Visible (UV-Vis) Spectroscopy

UV-Vis spectroscopy can investigate a wide variety of catalysts in both the liquid-phase and solid-state and interfaces thereof at elevated temperatures and pressures [6]. UV-Vis spectroscopy provides electronic details about materials. The Ligand-to-Metal-Charge Transfer (LMCT) bands inform about the molecular structural details of cations in high oxidation states (e.g.,  $\text{Re}^{+7}$ ,  $\text{W}^{+6}$ ,  $\text{Mo}^{+6}$ ,  $\text{Cr}^{+6}$ ,  $\text{Ta}^{+5}$ ,  $\text{Nb}^{+5}$ ,  $\text{V}^{+5}$ , etc.). Thus, the spectral features may be affected by intertwined factors during reaction (i.e., oxidation state and coordination and domain size). Additionally, the LMCT optical band gap or edge energy reflects the domain size of the cation (e.g., isolated, dimer, trimer, cluster, etc.) [7]. The corresponding d-d bands reflect the structure of cations in lower oxidation state (e.g.,  $\text{V}^{+4}$ ,  $\text{V}^{+3}$ ,  $\text{Cr}^{+5}$ ,  $\text{Cr}^{+3}$ ,  $\text{Ni}^{+4}$ ,  $\text{Ni}^{+2}$ , etc.). Complementary approaches are needed for precise spectral interpretation and are illustrated by the chapter by Zhu. Furthermore, UV-Vis spectroscopy can simultaneously measure electronic transitions of organic molecules and transition metal oxides or ions, thus reporting on the catalyst and reacting molecules. The strong UV-Vis signal allows for time-resolved measurements. The chapter by Weckhuysen et al. reports on this issue, and their hyphenation for studying spatial heterogeneities.

### Fluorescence Microscopy

Fluorescence is a highly sensitive spectroscopy that, combined with a convenient reporter, can be used to uncover important aspects of catalysis with high space and time resolution. Heterogeneous catalysts are indeed heterogeneous structurally and compositionally, and these profiles may change during reactions. The chapter by Chen et al. describes single-molecule fluorescence microscopy for real-time, spatially resolved characterization during catalysis. This chapter discusses characterization at the single-particle to sub-particle level, uncovering cooperativity between spatially distinct locations.

### Photoluminescence (PL) Spectroscopy

PL spectroscopy is highly sensitive to the environment of the cations, and it can report changes during catalytic reactions of molecules on catalysts and the interactions thereof. PL can directly report on the states of surface lattice oxide ions at various locations with different coordination numbers. The chapter by Anpo et al. describes this technique, and the chapter by Mino et al. covers several representative case studies applied to photocatalysis.

### X-ray Photoelectron Spectroscopy (XPS)

XPS surface analysis is extensively applied in heterogeneous catalysis to determine the quantitative composition and oxidation states of elements in the surface region (1–3 nm), the limited mean free path of the photoelectrons ejected from the sample as a result of the photoelectric effect. Traditional XPS studies are performed under UHV conditions, which can introduce experimental artifacts since surface cations can undergo reduction when exposed to x-ray irradiation under UHV conditions. This has resulted in many incorrect conclusions in the literature about the cation oxidation states in catalysts possessing reducible cations. Furthermore, a recent analysis of the XPS literature has found that 30% of the XPS publications have been incorrectly analyzed [8, 9]. Care must, thus, be made in collecting and analyzing

traditional XPS data collected under UHV conditions. UHV conditions can alter the pristine material surface further digressing from its real state during reaction conditions. The role of reactants and reaction temperature and representative pressures is critical to understanding the state of catalytic materials during the reaction. The recent introduction of near atmospheric pressure-XPS, however, allows operating under gas and liquid environments that minimize reduction of the cations during surface analysis, reporting on active phases and changes during the reaction, as the chapter by Rodríguez describes and further illustrated by the case studies in the chapter by Tao.

### **Electron Microscopies (EM)**

Scanning electron microscopy (SEM) gives an initial overview of catalytic materials by assessing their structural features and homogeneity: morphology, texture, particle size, bulk elemental composition, and uniformity at the micron scale. The SEM is also ideally suited to observe exposed surface facets in nanoparticles. The chapter by Datye and de la Riva illustrates these features.

While SEM is typically limited to the sample morphology, transmission electron microscopy (TEM) reveals bulk structural information of a sample. Environmental TEM characterization is currently possible by keeping part of the volume surrounding the sample under elevated pressure to perform high-pressure TEM. This enables the study under catalytically relevant conditions. The chapter by Foucher and Stach reviews high-pressure transmission electron microscopy by underlining relevant cases and delivering a perspective on the future way forward.

High-angle annular dark field (HAADF) imaging in the aberration-corrected scanning transmission electron microscope (AC-STEM) is a powerful characterization technique with good atomic number contrast and ultrahigh spatial resolution. Progress has also been made to analyze beam-sensitive samples. The chapter by He et al. further elaborates on HAADF imaging of catalysts in gaseous or liquid environments by illustrating *in situ* and *operando* case studies. The chapter by Li et al. illustrates a case study for  $\alpha$ -MoC-supported metal catalysts.

### **Low Energy Ion Scattering (LEIS)**

Low energy ion scattering (LEIS) is the most surface-sensitive technique providing quantitative elemental composition of the outermost surface layer ( $\sim 0.3$  nm). When coupled with sputtering, LEIS can also provide elemental composition as a function of the depth of the surface region ( $\sim 0.3$ – $5$  nm). Special attention must be paid to the possibility of preferential sputtering of certain cations. Traditional LEIS instruments are equipped with a detector that only collects a small fraction of the scattered ions, which results in weak signals that require collection times of several minutes. Consequently, the impinging ions sputter the surface during the measurement, and the resulting signals are averaged over the collection times (extent of sputtering). A recent development in the LEIS spectroscopy field has been the introduction of high sensitivity-LEIS (HS-LEIS) spectrometers that collect all the scattered ions and also employ time-of-flight filters to increase the intensity of the LEIS signals by  $\sim 3,000\times$  [10]. The increased signal intensity provided by the HS-LEIS spectrometer allows rapid analysis and minimizes elemental surface compositional artifacts introduced by sputtering from the primary ion beam. The chapter by Chen and Zheng illustrates the fundamentals and potential of LEIS, and the chapter by Wachs et al. illustrates several case studies (i.e., photocatalysts, bulk mixed oxides, bulk metals, supported metals, and supported metal oxides) where the knowledge of the outermost surface layer provides a direct relationship with catalytic performance that enables atomic understanding of structure-performance relationships.

### Neutron Scattering (NS)

Neutron scattering techniques deliver information about materials in different manners. The interaction of neutrons with matter may provide information on magnetic, vibrational excitations and molecular dynamics of catalysts and is also sensitive to different isotopes. The chapter by Ramírez-Cuesta et al. describes the different neutron-based techniques (neutron diffraction, inelastic neutron spectroscopy, or quasi-elastic neutron scattering) touching base on their advantages and limitations. Inelastic neutron scattering is the most utilized technique in catalysis, particularly for investigating the role of hydrogen-related species.

### X-ray Diffraction (XRD)

X-ray diffraction is used to determine the structure and particle size of crystalline materials. However, the crystalline phase must be greater than 3 nm to provide the long-range order information. This means that ultrasmall crystalline phases and 2D/3D amorphous phases cannot be detected with XRD. Sometimes it is claimed in the literature that a phase is amorphous if it is not detectable with XRD, which is incorrect since the crystalline phase may be present and smaller than 3 nm. Raman spectroscopy or TEM measurements are needed to confirm the absence or presence of crystalline phases smaller than 3 nm. The chapter by Kiani provides a thorough description of x-ray diffraction, origin, fundamentals, and pros and cons. The chapter also brings insight on how to overcome the limitations of XRD and its evolution to in situ and *operando* studies. The chapter by Beato et al. reports on XRD for process monitoring with an emphasis on zeolite synthesis. The chapter also covers the degree of crystallinity, crystallite size, and strain that allow for the study of defects. Highly crystalline materials also allow for fast *operando* XRD measurements. A perspective on comparison of conventional lab-based XRD and synchrotron-based XRD is also discussed.

### X-ray Absorption Spectroscopy (XAS): X-ray Absorption Near Edge Spectroscopy (XANES)/Extended X-ray Absorption Fine Structure (EXAFS)

X-ray absorption spectroscopic analysis of catalysts provides information about local coordination (XANES) and structural/cation oxidation state (EXAFS). A major problem encountered in the literature is that it is assumed that only one structure is present in the catalyst. If only one structure is present, then the XAS analysis will provide the coordination and local environment of the element under investigation. If multiple structures are present, however, XAS is unable to distinguish between multiple structures since it is an averaging technique (e.g., if both surface metal oxide sites and crystalline NPs are present in the catalyst). Thus, before collecting XAS spectra, it is important to determine if only one component is present in the catalyst or the structural information will be meaningless. With the growth of synchrotron facilities over the years and XAS studies becoming more common, this has become a serious issue since many of the reported molecular structures are corrupted because they may have more than one component.

The chapter by Newton et al. illustrates recent *operando* XAS studies, underlining recent developments in beamline, detector technology, cell designs, and experimental arrangements, with particular emphasis on electrocatalysis and photocatalysis, and also informs on possibilities for “soft” X-ray regime (x-rays with short attenuation lengths). The chapter by Weckhuysen et al. emphasizes developments in time-resolved X-ray absorption, sub-second X-ray absorption near-edge spectroscopy (XANES), to investigate the whole catalytic lifecycle in combination with 2D/3D imaging. The case study chapter by Ribeiro Passos et al. also illustrates time-resolved XAS as an approach to identify reaction intermediates and catalytic active sites with application of multivariate data analysis. This methodology is also relevant to the final chapter by Engel and Minnich on chemometrics, which is an increasingly important tool to process experimental data. The case study chapter by Zhang et al. on alloys provides insights about the determination of the composition, chemical and structural states of the

surface of alloy nanoparticles via isolation of the surface signal of the catalyst. This is particularly important since the catalytic active sites of heterogeneous catalysts are only present on the surface.

The chapter by Matras et al. focuses on synchrotron imaging analyses, reporting on chemical and structural imaging techniques underlining dynamic micro/macro interplays. The chapter by Becher et al. discusses 2D/3D XAS imaging techniques including imaging with absorption, fluorescence, or scattering contrast, spectroscopic imaging techniques such as XAS microscopy and tomography, and high-resolution imaging from the micro- to the nano-scale. The chapter by Agostini and Iglesias-Juez underlines cases where XAS is applied to catalyst preparation, characterization and reaction monitoring. Additionally, it shows the added value of combined complementary information from infrared that illustrates the enhanced value provided by multi-technique in situ and *operando* synchrotron studies.

### **Nuclear Magnetic Resonance (NMR)**

Nuclear magnetic resonance is a nondestructive spectroscopic technique that provides detailed molecular structural information of NMR active nuclei (e.g.,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{51}\text{V}$ , etc.), and the NMR signal quality increases with higher magnetic fields. The chapter by Hu et al. explains NMR and quadrupolar nuclei and covers the application of high-field NMR for aluminum- and vanadium-containing catalytic materials as well as covering NMR applications in catalysis and electrochemistry. High-field NMR is a very informative tool for many catalytic systems. There are, however, NMR nuclei with poor sensitivity that cannot be analyzed by amplification of the magnetic fields, and new approaches are needed, for instance, nuclei with low natural abundances or low gyromagnetic ratios, or nuclei with a large quadrupolar moment. The chapter by Lapina and Yakolev describes new advanced NMR techniques such as intricate pulse programs, correlation experiments, dynamic nuclear polarization, and selective isotope enrichment that provide state-of-the-art examples of tackling challenging issues for supported oxide catalysts, zeolites, and metal-organic frameworks (MOFs) materials. Combination of ultrahigh magnetic fields with selective isotopic enrichment of surface/near-surface layers enables investigating surface defects for high surface area materials. As for other characterization in other chapters in this handbook, combination with other characterization techniques and methodologies provides a more detailed perspective: density functional theory (DFT), molecular dynamics (MD), and other spectroscopic, microscopic, and diffraction methods. Examples of *operando* NMR are also covered in the chapters by Hu et al. and Lapina and Yakolev. A new dimension is added in the chapter by Koptug et al. that applies magnetic resonance imaging (MRI) and spatially resolved nuclear magnetic resonance (NMR) spectroscopy (MRS) to unravel information about processes inside the pores of heterogeneous catalysts and catalytic reactors, for instance, heat and mass transport processes, chemical composition profiles, and reaction conversion gradients. The chapter by Fraissard explains the use of hyperpolarized xenon ( $^{129}\text{Xe}$ ) for the study of the porosity of materials, location and loading of strong adsorption sites, surface structural defects, and distribution of adsorbed species, among others.

### **Electron Paramagnetic Resonance (EPR)**

Electron paramagnetic resonance measures the paramagnetism of species with unpaired electrons (e.g.,  $\text{Cr}^{5+}$ ,  $\text{Mo}^{5+}$ ,  $\text{W}^{5+}$ ,  $\text{V}^{4+}$ ,  $\text{Nb}^{4+}$ ,  $\text{Cr}^{+3}$ , etc., ions and free radicals). EPR is more regularly used under reactive conditions, and the experimental configuration of EPR instruments is particularly compatible with various ways of operating under *operando* conditions (such as plug flow fixed-bed reactor cells, in situ photolysis, and electrochemistry). The chapter by Walter presents a broad view of EPR and its capacities for in situ and *operando* studies; underlines multimodal in situ studies with complementary measurements – X-ray, beam-line techniques, and mass spectrometry; and also highlights the power of EPR engagement with NMR/DNP, which opens up a new scenario. The chapter by Mossin and Nielsen provides examples where materials are characterized under ex situ, in situ, and *operando* conditions

(selective catalytic reduction (SCR) reaction by copper-exchanged zeolites and vanadium-substituted polyoxometallate-derived materials on a titania support during in situ cycling between different gas mixtures relevant for the SCR reaction).

### **Transient Methods: Temporal Analysis of Products (TAP), Steady-State Isotopic Transient Kinetic Analysis (SSITKA), and Modulation Excitation Spectroscopy (MES)**

Catalysts are dynamic under reaction conditions and additional mechanistic insights can be provided by transient experiments by employing pulses of reactants, isotopic transients, and modulation of reactants (Temporal Analysis of Products (TAP), Steady-State Isotopic Transient Kinetic Analysis (SSITKA), and Modulation Excitation Spectroscopy (MES), respectively). The methodologies perturb the catalytic system to allow to distinguish between active species/sites and spectator species/sites. The chapter by Fushimi and Wang describes the TAP pulse response method to characterize kinetic properties and unravel mechanistic features. This chapter provides experimental and theoretical methodologies for TAP pulse response analysis. There are efforts to also implement *operando* TAP methodologies in combination with optical spectroscopy (Raman, IR, and UV-Vis). The chapter by Yang et al. describes the principles and methodology of SSITKA in heterogeneous catalysis where the catalyst is at steady state and only the isotope of one of the reactants is switched. Detailed analysis on how this switch is expressed in the reaction product isotope distribution is a powerful source of kinetic and mechanistic information. The calorimetry case study chapter by Polo-Garzón is also relevant to this section since it reports on a combined SSITKA-microcalorimetry study. MES is another transient dynamic method that allows discrimination between active and spectator species. MES operates by imposing periodic changes in reactant concentrations to the catalytic reactor, inducing a periodic perturbation of the active species/sites and reaction steps. Combining MES signals with phase-sensitive detection (PSD) analysis, it is possible to selectively enhance the responsive signals (active species/sites) while attenuating those from the non-responding signals (spectator species/sites). The chapter by Urakawa et al. describes the MES principles and procedures, experimental and analytical, touching base on specific examples and underlining experimental risks associated with the perturbation induced by the spectroscopic measurement. The chapter by Jeremiah et al. applies MES to the selective catalytic reduction (SCR) reaction and shows how stepping from steady state to modulated transient-response delivers new mechanistic insights, reports on weakly adsorbed responsive  $\text{NO}^+$ , resolves overlapping peaks ( $\text{NH}_3$  and  $\text{NH}_4^+$ ), or isolates the signal of the active/responsive species/sites (e.g., coordinatively unsaturated  $\text{VO}_x$  sites) from the stationary and catalytically inactive species/sites. The chapter by Briand and Collins brings an example of infrared spectroscopy in attenuated total reflection (ATR) to investigate enzymes at work in an optimized ATR flow-through cell that allows modulation excitation spectroscopy with phase-sensitive detection (MES-PSD). This method identifies signals associated with the interaction between ketoprofen and the lipase, showing that the acyl enzyme species is the key intermediate in the kinetic formation of profens. Transient techniques are a step forward for *operando* methodologies since they allow going beyond only examining the state of the catalyst and reactants during steady-state reaction conditions because they allow pinpointing the participating active species/sites in the catalytic cycle.

### **Temperature-Programmed (TP) Techniques**

Temperature-programmed techniques chemically probe the reactivity of functionalities present in the catalysts and their correlation with structural changes. An important aspect of TP techniques is that they can distinguish between multiple similar functionalities that may be present in the catalyst. For example, the chemical reactivity of an oxide catalyst can reveal the

presence of multiple oxygen sites with differing reactivity (e.g., during H<sub>2</sub>-temperature programmed reduction) or multiple adsorption sites with differing binding energies (e.g., during temperature programmed desorption or temperature programmed surface reaction). Another advantage of TP techniques is that they contain the intrinsic kinetics of the chemical event. The only downside is that if the TP bands are broad, then it may be difficult to distinguish between two distinct functionalities that may be present. The chapter by Jehng et al. provides an overview of TP techniques by covering the advantages, limitations, and appropriate experimental procedures.

### **Calorimetry**

Calorimetry measures heat associated with any adsorption or chemical process. The experimental instruments have become increasingly powerful and versatile so that they can be used to further understand the energetics of adsorption and reaction mechanisms by catalysts. The chapter by Silvester et al. provides the basic principles and the operation modes of calorimetric techniques (e.g., differential scanning calorimetry (DSC), calorimetry-volumetry (gas adsorption calorimetry), liquid phase calorimetry, and single crystal adsorption calorimetry (SCAC)). It provides a comprehensive fundamental and experimental insight into the energetics of adsorption and chemical reactions. The case study chapter by Polo-Garzón et al. describes the application of adsorption microcalorimetry to acid-base catalysis by mixed metal oxides. This case brings a common feature to most techniques in this handbook, the complementary of information from different approaches. The chapter shows how the combination of adsorption calorimetry with *ab initio* theoretical calculations explains the activation of a reactant on the surface of a mixed metal oxide catalyst. The chapter also combines steady-state isotopic transient kinetic analysis (SSITKA) with adsorption microcalorimetry to understand surface reconstruction phenomena, among others. The chapter by Yang et al. provides a detailed description of the SSITKA experimental and conceptual procedures, as described in the Transient Methods section.

### **Chemometrics to Enable “Soft *Operando*” Processing**

*Operando* studies do not end with the experiment since it is only the first part. The next step involves analyzing spectra and extracting information. The current progress in experimental techniques can deliver a multitude of spectra with high temporal, spatial, or any parameter resolution. Spectroscopic information is typically multiparametric, and, thus, it is important to have the right tools to extract useful information. The chapter by Engel and Minnich reports on chemometrics that enable analysis of *operando* data that we may think of as soft *operando* tools. The chapter presents and compares the most prominent methods: peak integration, spectral hard modeling, and projection to latent structures (PLS regression, also known as partial least-squares). These are applied to infrared, Raman, and NMR measurements and are formally transferable to any spectroscopic measurement. In addition to an analysis tool, these methods can also be used to generate a model that will directly convert spectral data into process data. This final chapter engages with all the previous chapters, providing the knowledge and toolbox to study chemical processes. In a broader vista, ultimately every characterization technique has to be harmonized, as we are already exploring in the European project CHARISMA for Raman spectroscopy (<https://www.h2020charisma.eu/>) [11]. Chemometrics is one of the pillars to ultimately allow quantitative comparisons of data taken by different equipment of a given characterization technique.

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**Part I**

**Vibrational Spectroscopy**



# Infrared (IR) Spectroscopy

1

Guido Busca

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## Abstract

The application of infrared (IR) spectroscopic methods in the field of heterogeneous catalysis research and development, mainly based on the original work of the author's group, is summarized. The fundamentals of vibrational spectroscopy are briefly described. The application of infrared spectroscopy in the catalyst skeletal region for structural characterization is considered. The spectra of pure powder-pressed discs of catalytic materials based

on oxides or supported with insulating carriers are described. In particular, data arising from the spectra in the OH stretching region (surface and bulk hydroxyl groups) are considered. The absorptions due to the vibrations of surface metal-oxygen bonds are discussed. The use of infrared spectroscopy of surface molecular probes for the characterization of surface acid sites both of the Lewis and the Brønsted type is considered. The application of molecular probes for the infrared characterization of surface basicity and nucleophilicity is also taken into account. Finally, the use of probes for the characterization of the redox state of the surface as well as of the size/shape of metal nanoparticles is also considered. The application of IR spectroscopy for the analysis of reaction products is also briefly discussed.

## Keywords

Infrared spectroscopy · Absorption · Scattering · Diffusion · Surface · Acidity · Basicity · Redox · Metals · Oxides

## 1.1 Introduction

After a pioneering application in 1937 by Buswell et al. [1], who reported the spectra of water adsorbed on montmorillonite, the very first systematic studies concerning infrared spectroscopy applied to solid surfaces are due to Alexander N. Terenin and his pupils working at the University of Leningrad (now St. Petersburg) in the 1940s and 1950s [2]. This technique rapidly found interest in industry, as evidenced by the work of Robert P. Eischens et al. at Texaco (Beacon, New York) in the 1950s [3] and later by John Peri at Amoco [4] and Edward P. Parry at Union Oil Company of California [5].

The research in this area anticipated and introduced the “surface science” research field, starting in the 60s and

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