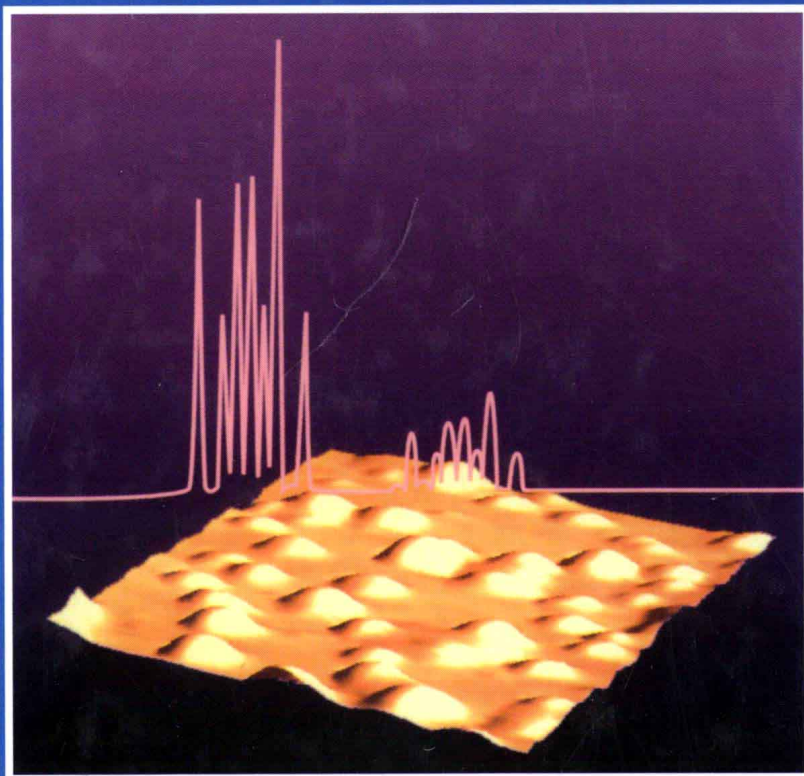


J. W. Niemantsverdriet

Spectroscopy in Catalysis

An Introduction

Second, Completely
Revised Edition



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Cover Illustration: Atomic force microscopy image of molybdenum oxide particles on flat, silicon dioxide substrate, which serves as a model system for a supported catalyst. The area shown corresponds to one square micrometer: the maximum difference in height is approximately 10 nanometer. The superimposed curve is the secondary ion mass spectrum of the model catalyst, showing the characteristic isotopic patterns of single molybdenum ions and of molybdenum oxide cluster ions.

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J. W. Niemantsverdriet

Spectroscopy in Catalysis

 **WILEY-VCH**

*To Marianne,
Hanneke, Annemieke,
Karin and Peter*

Preface

‘Spectroscopy in Catalysis’ is an introduction to the most important analytical techniques that are nowadays used in catalysis and in catalytic surface chemistry. The aim of the book is to give the reader a feeling for the type of information that characterization techniques provide about questions concerning catalysts or catalytic phenomena, in routine or more advanced applications.

The title ‘Spectroscopy in Catalysis’ is attractively compact but not quite precise. The book also introduces microscopy, diffraction and temperature programmed reaction methods, as these are important tools in the characterization of catalysts. As to applications, I have limited myself to supported metals, oxides, sulfides and metal single crystals. Zeolites, as well as techniques such as nuclear magnetic resonance and electron spin resonance have been left out, mainly because the author has little personal experience with these subjects. Catalysis in the year 2000 would not be what it is without surface science. Hence, techniques that are applicable to study the surfaces of single crystals or metal foils used to model catalytic surfaces, have been included.

The book has been written as an introductory text, not as an exhaustive review. It is meant for students at the start of their Ph.D. projects and for anyone else who needs a concise introduction to catalyst characterization. Each chapter describes the physical background and principles of a technique, a few recent applications to illustrate the type of information that can be obtained, and an evaluation of possibilities and limitations. A chapter on case studies highlights a few important catalyst systems and illustrates how powerful combinations of techniques are. The appendix on the surface theory of metals and on chemical bonding at surfaces is included to provide better insight in the results of photoemission, vibrational spectroscopy and thermal desorption.

Finally, an important starting point was that reading the book should be enjoyable. Therefore, the book contains many illustrations, as few theoretical formulas as possible and no mathematical derivations. I hope that the book will be useful and that it conveys some of the enthusiasm I feel for research in catalysis.

About the Second Edition

The present version of the book represents a completely revised update of the first edition as it appeared in 1993. Significant new developments in *e.g.* the scanning probe microscopies, imaging and vibrational techniques called for revision and additions to the respective chapters. But also the other chapters have been updated with recent examples, and references to relevant new literature. Many figures from the first version of the book have been improved to make them more informative. The chapter with case studies has been expanded with an example on polymerization catalysts.

Since its publication I have used the book as an accompanying text in courses on catalyst characterization, both at the Eindhoven University of Technology and the Netherlands Institute for Catalysis Research, NIOK. It has been very rewarding to learn that several colleagues in catalysis have adopted the book for their courses as well. I will be very grateful for comments and corrections. Colleagues who are interested in the exercises we use at Eindhoven are most welcome to contact me, the set is available at nominal cost.

Acknowledgements

When I obtained my Masters Degree in experimental physics at the Free University in Amsterdam in 1978, I was totally unaware that as interesting an area as catalysis, with so many challenges for the physicist, existed. I am particularly grateful to Adri van der Kraan and Nick Delgass who introduced me, via the Mössbauer Effect in iron catalysts, to the field of catalysis. My Ph.D. advisors at Delft, Adri van der Kraan, Jan van Loef and Vladimir Ponec (Leiden), together with Roel Prins from Eindhoven, stimulated and helped me to pursue a career in catalysis, now about seventeen years ago.

All these years, Eindhoven has been a stimulating environment. Working with Rutger van Santen, Diek Koningsberger, Roel Prins, Dick van Langeveld, Jan van Hooff, San de Beer, Theo Beelen, Barbara Mojet, Tonek Jansen, Rob van Veen, Bruce Anderson, Gert-Jan Kramer and Marc Koper and outside our own laboratory Hidde Brongersma, Kees Flipse, Guy Marin, Piet Lemstra, Martien de Voigt, Leo van IJzendoorn and Peter Hilbers has been a great experience. It is a pleasure to mention pleasant and fruitful collaborations with Nick Delgass, Steen Mørup, Klaus Wandelt, Fabio Ribeiro and Gabor Somorjai, who taught me a lot over the years. I gratefully acknowledge the generous financial support of 'Huygens' and 'Pionier' fellowships from the Netherlands Organization for Scientific Research (NWO).

This book contains many examples taken from a group of people with whom I worked at the Eindhoven University of Technology. I thank Herman Borg, Leon Coulier, Andre Engelen, Lyn Eshelman, Wouter van Gennip, Leo van Gruijthuijsen, Pieter Gunter, Martijn van Hardeveld, Marco Hopstaken, Ton Janssens, Arthur de Jong, Gurram Kishan, Hanna Korpik, Ralf Linke, Joachim Loos, Stefan Louwers, Toon Meijers, Hannie Muijsers, Leon van den Oetelaar, Joost Reijerse, Arno Sanders, Elina Siokou, Peter Thüne, Rik van Veen, Tiny Verhoeven, Thomas Weber and many others for the very pleasant and fruitful collaboration we have had.

I am grateful to Paul Weymans for drawing several complicated figures and to Tiny Verhoeven for solving several computer problems.

Finally, I want to thank my wife Marianne, our daughters Hanneke, Annemieke, Karin and our son Peter for the many weekends and evenings they patiently allowed me to work on this book. I dedicate this book to them.

Eindhoven, January 2000

Hans Niemantsverdriet

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1 Introduction

Heterogeneous Catalysis
Aim of Catalyst Characterization
Spectroscopic Techniques
Research Strategies

1.1 Heterogeneous Catalysis

Catalysis plays a prominent role in our society. The majority of all chemicals and fuels produced in the chemical industry have been in contact with one or more catalysts. Catalysis has become indispensable in environmental pollution control: selective catalytic routes are replacing stoichiometric processes that generate waste problems. The three-way catalyst effectively reduces pollution from car engines. Catalytic processes to clean industrial exhaust gases have been developed and installed. In short, catalysis is vitally important for our economy now, and it will be even more important in the future.

A heterogeneous catalytic reaction begins with the adsorption of the reacting gases on the surface of the catalyst, where intramolecular bonds are broken or weakened. The Appendix explains how this happens on metals in terms of simplified molecular orbital theory. Next, the adsorbed species react on the surface, often in

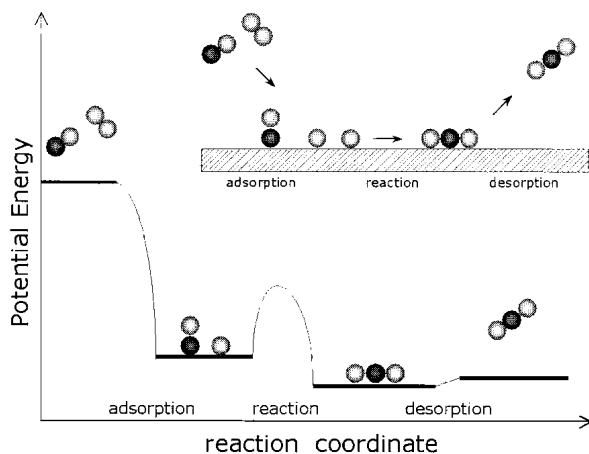


Figure 1.1: Schematic representation of a well known catalytic reaction, the oxidation of carbon monoxide on noble metal catalysts: $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$. The catalytic cycle begins with the associative adsorption of CO and the dissociative adsorption of O_2 on the surface. As adsorption is always exothermic, the potential energy decreases. Next CO and O combine to form an adsorbed CO_2 molecule, which represents the rate-determining step in the catalytic sequence. The adsorbed CO_2 molecule desorbs almost instantaneously, thereby liberating adsorption sites that are available for the following reaction cycle. This regeneration of sites distinguishes catalytic from stoichiometric reactions.

several consecutive steps. Finally, the products desorb from the surface into the gas phase, thereby regenerating the active sites on the surface, ready for the next catalytic cycle. The function of the catalyst is to provide an energetically favorable pathway for the desired reaction, in which the activation barriers of all intermediate steps are low compared to the activation energy of the gas phase reaction. Figure 1.1 illustrates the sequence for the catalytic oxidation of carbon monoxide. Here the key role of the catalyst is to dissociate the O_2 molecule – a process that can occur on many metal surfaces. Some introductory texts on the theory of catalysis are listed in the references [1–12].

As catalysis proceeds at the surface, a catalyst should preferably consist of small particles with a high fraction of surface atoms. This is often achieved by dispersing particles on porous supports such as silica, alumina, titania or carbon (see Fig. 1.2). Unsupported catalysts are also in use. The iron catalysts for ammonia synthesis and CO hydrogenation (the Fischer–Tropsch synthesis) or the mixed metal oxide catalysts for production of acrylonitrile from propylene and ammonia form examples.

Catalysts may be metals, oxides, zeolites, sulfides, carbides, organometallic complexes, enzymes, etc. The principal properties of a catalyst are its activity, selectivity, and stability. Chemical promoters may be added to optimize the quality of a catalyst, while structural promoters improve the mechanical properties and stabilize the particles against sintering. As a result, catalysts may be quite complex. Moreover, the state of the catalytic surface often depends on the conditions under which it is used. Spectroscopy, microscopy, diffraction and reaction techniques offer tools to investigate what the active catalyst looks like.

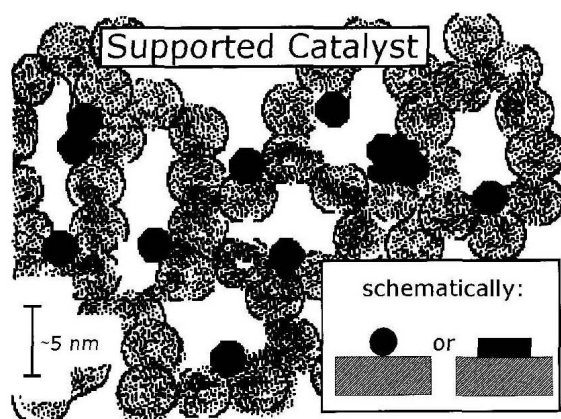


Figure 1.2: Impression of a silica-supported catalyst; the inset shows the usual schematic representations.

1.2 Aim of Catalyst Characterization

The catalytic properties of a surface are determined by its composition and structure *on the atomic scale*. Hence, it is not sufficient to know that a surface consists of a metal and a promoter, say iron and potassium, but it is essential to know the exact structure of the iron surface, including defects, steps, etc., as well as the exact locations of the promoter atoms. Thus, from a fundamental point of view, the ultimate goal of catalyst characterization should be to look at the surface atom by atom, and under reaction conditions. The well-defined surfaces of single crystals offer the best likelihood of atom-by-atom characterization, although occasionally atomic scale information can be obtained from real catalysts under *in situ* conditions as well, as the examples in Chapter 9 show.

The industrial view on catalyst characterization is different. Here the emphasis is mainly on developing an active, selective, stable and mechanically robust catalyst. In order to accomplish this, tools are needed which identify those structural properties that discriminate between efficient and less efficient catalysts. All spectroscopic information that helps to achieve this is welcome. Establishing empirical relationships between the factors that govern catalyst composition, particle size and shape and pore dimensions on the one hand and catalytic performance on the other are extremely useful in the process of catalyst development, although such relationships may not give much fundamental insight into how the catalyst operates in molecular detail.

Van Santen [13] identifies three levels of research in catalysis. The *macroscopic* level is the world of reaction engineering, test reactors and catalyst beds. Questions concerning the catalyst deal with such aspects as activity per unit volume, mechanical strength and whether it should be used in the form of extrudates, spheres or loose powders. The *mesoscopic* level comprises kinetic studies, activity per unit surface area, and the relationship between the composition and structure of a catalyst and its

catalytic behavior. Much characterization work belongs to this category. Finally, the *microscopic* level is that of fundamental studies and deals with the details of adsorption on surfaces, reaction mechanisms, theoretical modeling and surface science.

Simplifying, one could say that catalyst characterization in industrial research deals with the *materials science of catalysts* on a more or less mesoscopic scale, whereas the ultimate goal of fundamental catalytic research is to characterize the surface of a catalyst at the microscopic level, *i.e.* on the *atomic* scale.

Catalyst characterization is a lively and highly relevant discipline in catalysis. A literature survey identified over 4000 scientific publications on catalyst characterization in a period of two years [14]. The desire to work with defined materials is undoubtedly present. No less than 78% of the 143 papers presented orally at the 11th International Congress on Catalysis [15] contained at least some results on the catalyst(s) obtained by characterization techniques, whereas about 20% of the papers dealt with catalytic reactions over uncharacterized catalysts. Another remarkable fact from these statistics is that about 10% of the papers contained results of theoretical calculations. The trend is clearly to approach catalysis from many different viewpoints with a combination of sophisticated experimental and theoretical tools.

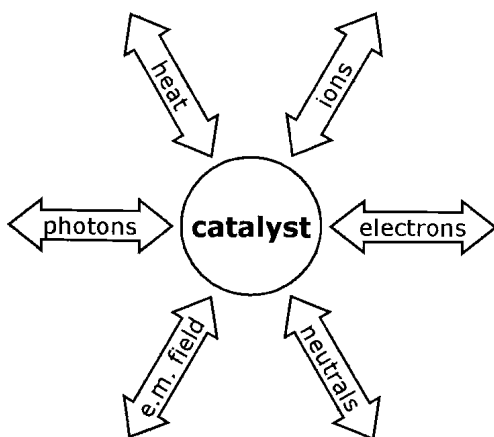


Figure 1.3: Diagram from which most characterization techniques can be derived. The circle represents the sample under study, the inward arrow stands for an excitation, and the outward arrow indicates how the information should be extracted.

1.3 Spectroscopic Techniques

There are many ways to obtain information on the physico-chemical properties of materials. Figure 1.3 presents a scheme from which almost all techniques can be derived. Spectroscopies are based on some type of excitation, represented by the ingoing arrow in Fig. 1.3, to which the catalyst responds as symbolized by the outgoing arrow. For example, one can irradiate a catalyst with X-rays and study how the X-rays are diffracted (X-ray diffraction, XRD), or one can study the energy distribution of electrons that are emitted from the catalyst as a result of the photoe-

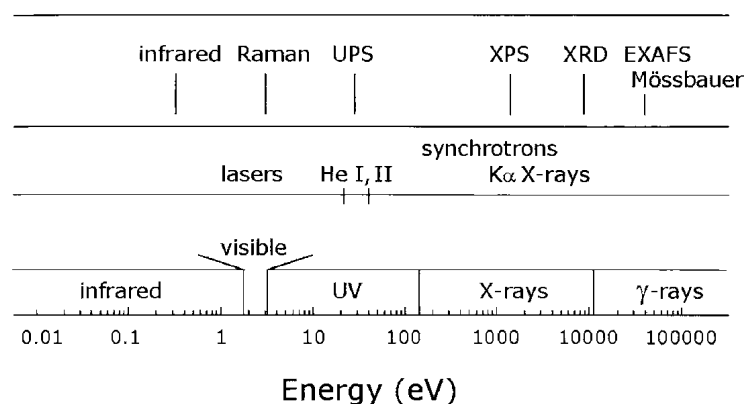


Figure 1.4: The electromagnetic spectrum, along with common photon sources and a number of characterization techniques based on photons.

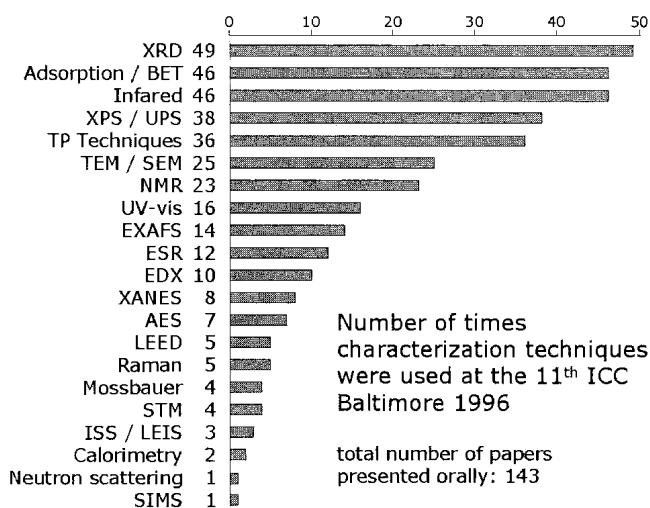


Figure 1.5: Bar diagram showing how often techniques have been used in the 143 orally presented papers at the 11th International Congress on Catalysis in Baltimore, 1996 [15].

lectric effect (X-ray photoelectron spectroscopy, XPS). One can also heat up a spent catalyst and look at the temperatures at which reaction intermediates and products desorb from the surface (temperature programmed desorption, TPD).

Characterization techniques become surface sensitive if the particles or radiation to be detected come from the outer layers of the sample. Low energy electrons, ions and neutrals can only travel over distances between one and ten interatomic spacings in the solid state, implying that such particles coming off a catalyst reveal surface-specific information. The inherent disadvantage of the small mean free path is that measurements need to be carried out in vacuum, which conflicts with the wish to investigate catalysts under reaction conditions.

Photons that are scattered, absorbed or emitted by a catalyst form a versatile source of information. Figure 1.4 shows the electromagnetic spectrum, along with a number of techniques involving photons. In addition to the common sources of photons (lamps, lasers, helium discharge and X-ray sources) available for laboratory

use, synchrotrons offer a broad spectrum of highly intense, polarized light. Electromagnetic radiation penetrates solids significantly. However, if the solid responds by emitting electrons, as in the photoelectric effect, one nevertheless obtains surface-specific information.

In this book we describe some of the most often used techniques in catalyst characterization (see Fig. 1.5). We will highlight those methods that have been particularly useful in the study of metal, oxide and sulfide catalysts, and related model systems. Zeolites and techniques such as nuclear magnetic resonance [2,3,16] fall outside the scope of this book. A number of books on catalyst characterization are listed in the references [3, 16–22].

1.4 Research Strategies

Keeping in mind that the aim of characterization in fundamental catalysis is to obtain information of the active surface under reaction conditions in molecular detail, one might think that surface science is the discipline that offers the best opportunities. However, many of the tools do not work on technical catalysts, and one has to resort to model systems. For example, one can model the catalytic surface with that of a single crystal [5]. By using the appropriate combination of surface spectroscopies, the desired characterization on the atomic scale is certainly possible in favorable cases. The disadvantage, however, is that although one may be able to study the catalytic properties of such samples under realistic conditions (pressures of 1 atm or higher), most of the characterization is necessarily carried out in ultrahigh vacuum and not under reaction conditions.

The other approach is to study real catalysts with *in situ* techniques such as infrared and Mössbauer spectroscopy, EXAFS and XRD, either under reaction conditions, or, as is more often done, under a controlled environment after quenching the reaction.

The *in situ* techniques, however, are usually not sufficiently specific to yield the desired atom-by-atom characterization of the surface. Often they determine overall properties of the particles. The situation is schematically represented in Fig. 1.6.

The dilemma is thus that investigations of real catalysts under relevant conditions by *in situ* techniques give little information on the surface of the catalyst, and that the techniques which are surface sensitive can often only be applied on model surfaces under vacuum. Model catalysts consisting of particles on flat, conducting supports sometimes offer an alternative with respect to surface analysis [23–27], as several examples in this book show. Also, *in situ* tools that work on single crystals or model surfaces can in some cases be used to assess the significance of results obtained in vacuum for application in the real world [28]. Bridging the gap between UHV and high pressure, as well as the gap between the surface of a single crystal and that of a real catalyst, are important issues in catalysis.

	real catalyst	single crystal
reaction conditions	XRD, TP techniques Infrared and Raman EXAFS, Mossbauer esr, NMR, AFM	Infrared TP techniques STM,AFM
vacuum	XPS, SIMS, SNMS LEIS, RBS, TEM, SEM	all surface science techniques

Figure 1.6: Possibilities for spectroscopic research in catalysis.

that both catalysis and spectroscopy are disciplines that demand considerable expertise. For instance, the state of a catalyst depends, often critically, on the method used to prepare it, its pretreatment or its environment. It is therefore essential to investigate a catalyst under carefully chosen, relevant conditions and after the proper treatment. Catalytic scientists know these things precisely.

Spectroscopy, too, is by no means simple. Quick and easy experiments in catalyst characterization hardly exist. The correct interpretation of spectra requires experience based on practice and a sound theoretical background in spectroscopy, in physical chemistry and often in solid state physics as well. Intensive cooperation between spectroscopists and experts in catalysis is the best way to ensure meaningful and correctly interpreted results.

It is good to realize that, although many techniques undoubtedly provide valuable results on catalysts, the most useful information almost always comes from a combination of several characterization techniques. The case studies in Chapter 9 present a few examples where this approach has been remarkably successful.

In conclusion, a successful outcome to any research on catalysts is most likely to be achieved by using a combination of spectroscopic techniques applied under conditions as close as possible to those of the reaction in which the catalyst operates and also by using an integrated approach in which experts from catalysis and spectroscopy work closely together.

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