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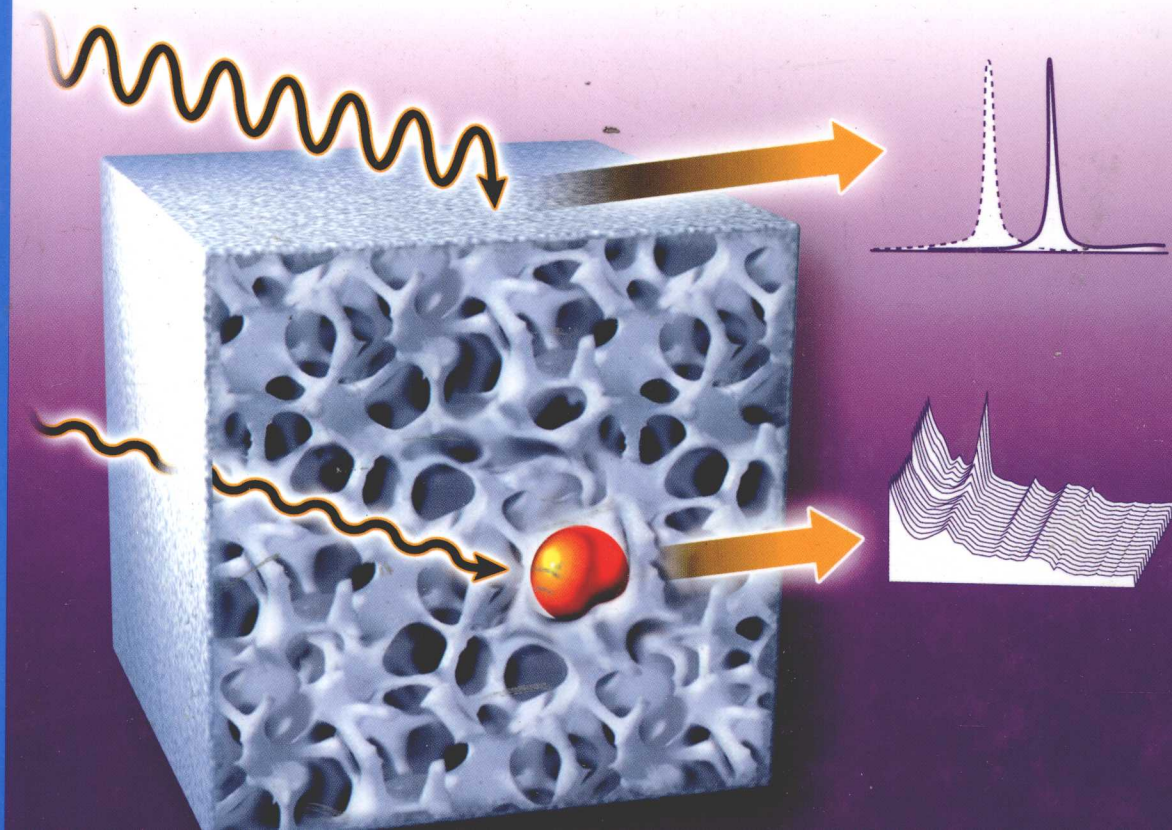
Characterization of Solid Materials and Heterogeneous Catalysts

From Structure to Surface Reactivity

Volume 2



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For our mentor Dr. Boris Imelik, and our Families

About the Editors

Michel Che

After a chemical engineering degree from Ecole Supérieure de Chimie Industrielle (Lyon, F), M. Che joined the Institut de Recherches sur la Catalyse (Lyon) as member of CNRS (National Center of Scientific Research). After a Doctorat ès Sciences in 1968 (Université de Lyon), he was postdoctoral fellow (1969-1971) at Princeton University. Between 1972 and 1982, he frequently worked as visiting scientist at the Atomic Energy Research Establishment at Harwell (UK). He became Professor at Université Pierre & Marie Curie-Paris 6 in 1975, and Senior Member of Institut Universitaire de France in 1995.

His research concerns the reactivity of solid surfaces investigated from a molecular standpoint based on the combined use of transition metal complexes, specific isotopes and physical techniques. His work, which led to 450 publications and 5 patents, has contributed to improve our understanding of the elementary processes developing at solid/liquid (gas) interfaces and to bridge the gap between homo- and heterogeneous catalysis.

Michel Che was President-Founder of EFCATS, the European Federation of Catalysis Societies (creating the biennial EuropaCat congresses), and later President of the International Association of Catalysis Societies. He received awards in France (A. Joannides and P. Sue), Netherlands (J. H. Van't Hoff), Poland (M. Sklodowska-Curie & P. Curie lectureship), Germany (Von Humboldt - Gay-Lussac Award, and GDCh Grignard-Wittig lectureship), UK (RSC Centenary lectureship), USA (Frontiers in Chemical Research lectureship, Texas), Japan (Japanese Society for the Promotion of Science lectureship), China (Gold Medal of Chinese Academy of Sciences, Friendship Award and International Science and Technology Cooperation Award) and Europe (François Gault EFCATS lectureship). His work earned him several honorary doctorates and fellowships (German Academy of Sciences-Leopoldina, Academia Europaea, Hungarian Academy of Sciences, Polish Academy of Arts and Sciences).

Jacques C. Védrine

After a chemical engineering degree from Ecole Supérieure de Chimie Industrielle (Lyon, F), J.C. Védrine joined the Institut de Recherches sur la Catalyse (IRC) in Lyon as member of CNRS. After a Docteur ès Sciences degree in 1968 (Université de Lyon), he was post-doc in USA at Varian Ass., Palo Alto (1969-1970) and Princeton University (1970-1971). He then returned to IRC and became deputy director in 1988. In 1998, he moved to the University of Liverpool, UK as Chair Professor and Deputy Director of the Leverhulme Centre for Innovative Catalysis. In 2003, he returned to France and was chargé de mission at the Ministry of National Education and Research. In 2006, he joined the Laboratory of Surface Reactivity at Université Pierre & Marie Curie, Paris.

His scientific interests cover heterogeneous catalysis, especially selective oxidation on mixed metal oxides, acid catalysis on oxide-based systems and acidity strength and nature determination. He worked on combinatorial catalysis (high throughput technique) and contributed in the 1990s to the EUROCAT group activities in standardizing heterogeneous catalyst characterization. He co-authored over 350 publications and a few patents, and co-edited 7 books. He is one of the Editors of Appl. Catal. A: General.

One of his major contributions was to organize in the 1980s regular training sessions to help researchers use complementary physical techniques to improve the characterization of solid catalysts, including under working conditions. This led to two books on Physical Characterization of Solid Catalysts (Technip, Paris, 1988 and Plenum Press, New York, 1994).

He was awarded the Grand Prix Pierre Sue of the French Chemical Society (SCF) in 2001. He was elected President of Catalysis Division of SCF (1994-1997), President of EFCATS (1997-1999) and President of the Acid-Base World Organization (2005-2009). He holds honorary doctorate from the University of Lisbon.

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Preface

Michel Che and Jacques C. Védrine

The spectacular progress achieved in chemistry is largely due to the use of physical techniques implemented at the level of the element, molecule, or phase with reliability and accuracy unattainable a few decades ago. Moreover, microscopic (molecular) and macroscopic (molar) information can be obtained by small-scale and often non-destructive experiments. Many of these techniques are now in routine use, essentially because of the progress of technology and availability of always more powerful and user-friendly computers.

We therefore thought that it was timely to provide a survey of the major techniques used to characterize solid materials and investigate their surface reactivity, a domain of chemistry, relevant to a variety of fields including adsorption, geochemistry, coatings, electrochemistry, corrosion, formation of biofilms, toxicity and catalysis. Those fields however do not require the same surface reactivity: for corrosion, the latter has to be inhibited, or even suppressed, because of its dramatic consequences on metals, while for catalysis not only it has to be enhanced but also selectively oriented to obtain the desired product.

From all the fields related to surface reactivity, catalysis appears to be unique because i) it has a large industrial impact, ii) it lies at the core of chemistry, i.e., starting with chemistry to prepare the catalytic system and ending with chemistry to promote a specific reaction, and iii) it involves physical and chemical processes developing mostly at liquid-solid, solid-solid, and/or gas-solid interfaces present at the successive steps of catalyst life, from its preparation to its use in the catalytic reaction. For those reasons, catalysis will be used as the directing thread of this book.

Investigations on solid materials have shown that their surfaces may change with the chemical environment to which they are exposed and that the more divided the solid, the more reactive it becomes. This book title illustrates this paradigm, with its dual aspects, the structure of the material on one hand and its surface reactivity on the other. For instance, for metals, it is known that metal-metal bond distances at the surface often contract under vacuum with respect to the bulk, while they relax in the presence of gaseous molecules reaching values close to those characteristic of the bulk. For alloys or mixed oxides, surface enrichment in one component is often

observed under reaction conditions. For some reactions, e.g. selective oxidation of olefins on metal oxide catalysts, the surface atoms of the solid catalyst may react, and even be incorporated into reactant molecules. For such redox-type reactions, surface atoms have to be mobile enough to allow the redox process to occur.

This book is intended to consider all those aspects with the objective to offer a general survey on the "Characterization of Solid Materials: From Structure to Surface Reactivity", useful to junior and senior research scientists, engineers and industrialists. We deemed it essential to present a portofolio of the techniques most frequently used and to dwell on those which appear to be most promising. For this reason, the space allocated to each chapter is different. Although still used, some techniques are not discussed in this book, because little improvement has been achieved since the publication of earlier books in 1988 [1] and 1994 [2].

Because of the large number of chapters/authors, consistency and homogeneity were felt to be essential. Therefore, the following format was suggested to authors:

1) Introduction covering the discovery and development of the technique,
2) Description of the basic phenomenon with a theoretical background including, where appropriate, its dimension/time/energy scales, energy states, terminology, units (those conventionally used in the field but also SI units), the strategy used and the essential parameters necessary to interpret experimental data,
3) Experimental considerations/constraints, relative to the characterization technique and to the surface reactivity,
4) Uses of the technique for the characterization of both model and real solid materials at different stages of their life (i.e., during preparation, functionalization, chemical or thermal activation, surface reactivity) with emphasis on the coupling with other techniques with its advantages and disadvantages,
5) Key examples of application of the technique to surface reactivity. For the field of catalysis, the reaction, deactivation, ageing, and regeneration steps had to be considered with emphasis on the identification and implication of intermediates in reaction mechanisms,
6) Conclusions including information gained with the technique, its advantages, limitations, and latest developments,
7) References.

We have tried to offer a book presenting a unique set of features:

- it deals with an ensemble of physical techniques commonly used at present to i) characterize solid materials and ii) investigate their surface reactivity,
- it provides overviews written by two outstanding scholars who have largely contributed to the development of physical techniques to investigate solid materials (single crystals and porous catalysts),
- each chapter aims at being both general and concise enough for the readers to understand the technique, and the meaning of the essential key parameters,
- it gives general data for each technique, with its historical background, domains of energy involved, spatial and time resolution, experimental constraints

(vacuum or presence of gaseous phase, temperature,...), atomic/molecular or macroscopic aspects,

- it emphasises the characterization of the solid material throughout its life: from its preparation to its application in surface reactivity-related domains,
- it includes the use of both experimental and theoretical approaches as a guide in designing experiments and interpreting results,
- it deals with both model and real solid materials,
- it aims at being a toolbox from which any researcher should be able to find the appropriate technique(s) for solving a specific problem.

To conclude, this book aims at being pedagogical, illustrative and practical, hoping that after having read the book, the reader be in a position to identify the most appropriate technique(s) able to answer his questions.

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General Introduction

Michel Che and Jacques C. Védrine

The two main goals of the book are to show how physical techniques can be used to characterize solid materials and to investigate their surface reactivity. The first goal corresponds to establishing the "identity card" of the material, including its structure, morphology, porosity, and chemical composition, and the second to obtaining characteristics of the surface related to its reactivity (nature and number of surface sites, subsequent modification upon functionalization, nature and number of adsorbed species and possible intermediates in surface-promoted phenomenon/reaction).

1
Basic Phenomenon and Classification of Physical Techniques

All techniques are based on the same phenomenon, often referred to as the Propst diagram (Figure 1): an incident beam hits the sample, giving rise to an emitted beam which is detected and analyzed because of the information it contains, leading to the "fingerprint" of the solid and/or of species or reaction intermediates adsorbed on it. The incident beam can be composed of photons, electrons, ions, neutrals, or magnetic, electric, acoustic, or thermal fields, and also the emitted beam.

Table 1 presents the main acronyms of the physical techniques presented or mentioned in this book and Table 2 gives the classification of typical techniques as a function of the nature of the incident and emitted beams. In Table 2, one distinguishes the diagonal techniques, for which incident and emitted beams are identical in nature and the information comes from the analysis of the modifications in intensity, energy, or frequency of the incident beam, from the off-diagonal techniques (shaded areas) for which those two beams are different in nature [2].

Table 3 lists the main spectroscopic techniques and associated events as a function of the characteristics of the incident beam (energy, domain of the electromagnetic spectrum, wavelength, and frequency).

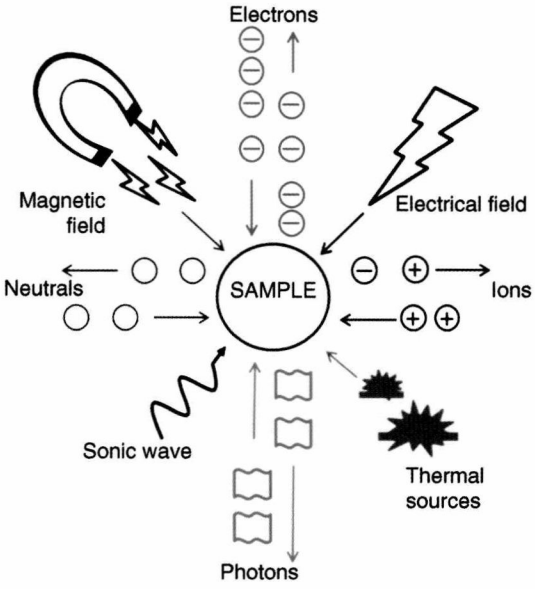

Figure 1 Basic phenomenon of physical techniques. The incident beams are defined by arrows oriented towards the sample while the emitted beams are defined by arrows oriented away from the sample. Adapted from [1].

Table 1 Acronyms and names of the techniques presented or mentioned in this book.

Acronym	Technique
AA	atomic absorption
AC-EM	aberration-corrected-electron microscopy
ADF	annular dark field
AES	Auger electron spectroscopy
AFM	atomic force microscopy
AIUP	angle-integrated ultraviolet spectroscopy
APS	appearance potential spectroscopy
ATR	attenuated total reflection
CEMS	conversion electron Mössbauer spectroscopy
CL	cathodoluminescence
CTEM	conventional transmission electron microscopy
CV	cyclic voltammetry
DFT	density functional theory
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
DRUV-vis	diffuse reflectance UV-vis
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTG	differential thermogravimetry
ED	electron diffraction
EDS	energy-dispersive spectroscopy
EDX	energy-dispersive X-ray
EELS	electron energy loss spectroscopy