Edited by Jean-Marie Basset, Rinaldo Psaro, Dominique Roberto, Renato Ugo

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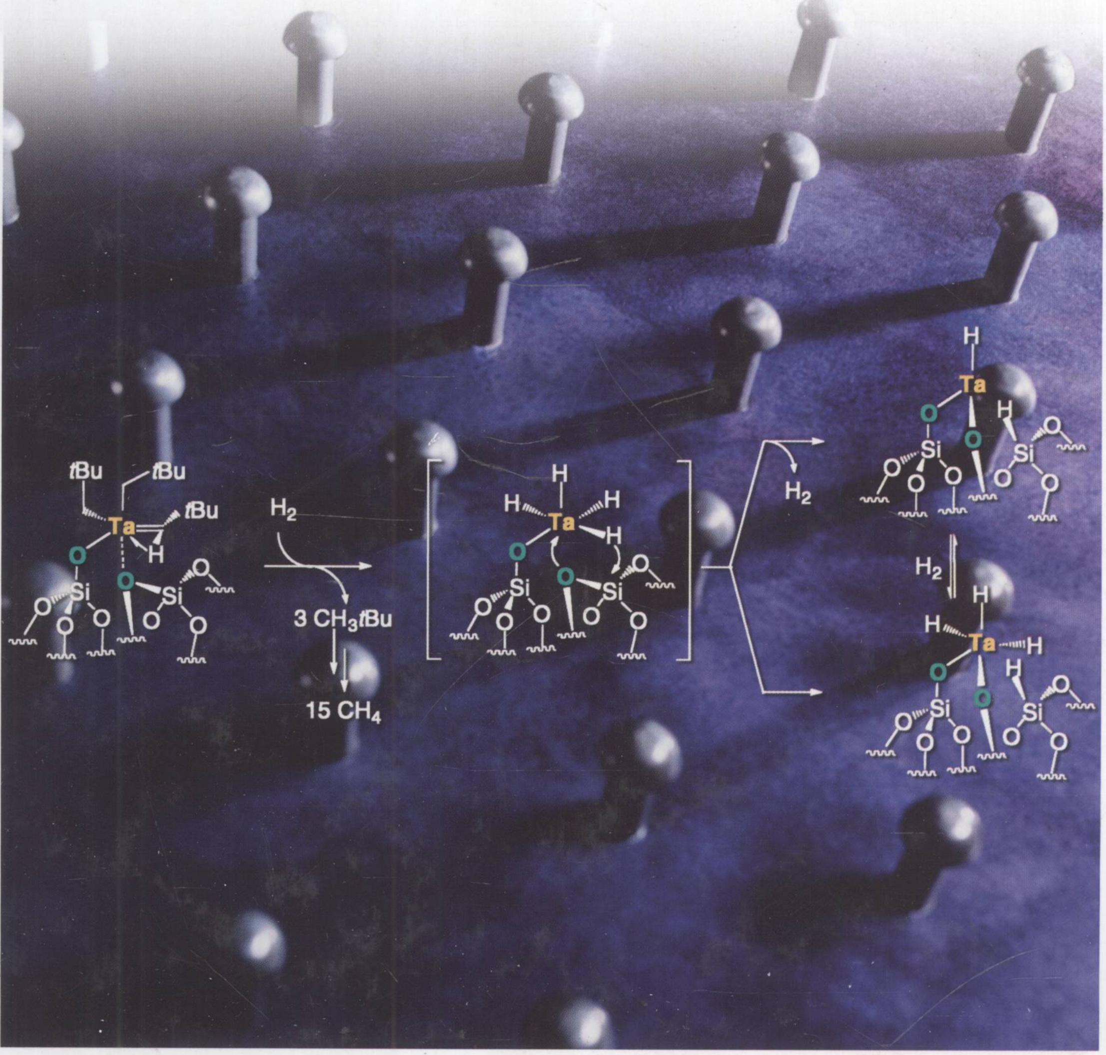

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The Editors

Prof. Dr. Jean-Marie Basset
Laboratoire de Chimie Organométallique de Surface
C2P2-UMR 5265 CNRS-CPE Lyon-UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69622 Villeurbanne Cedex
France

Dr. Rinaldo Psaro
CNR, Institute of Molecular Sciences and Technologies (ISTM)
Via Golgi 19
20133 Milano
Italy

Prof. Dr. Dominique Roberto
Università di Milano
Dipartimento di Chimica Inorganica Metallorganica e Analitica "Lamberto Malatesta"
via G. Venezian 21
20133 Milano
Italy

Prof. Dr. Renato Ugo
Università di Milano
Dipartimento di Chimica Inorganica Metallorganica e Analitica "Lamberto Malatesta"
via G. Venezian 21
20133 Milano
Italy

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Preface

Catalysis is the number one technology in chemical industry and petroleum refining. In the future one may reasonably expect that catalysis will be among the leading solutions for meeting the new global and intimately related challenges of environment and energy. The advantages of catalytic processes are due to the relatively mild reaction conditions, their cost efficiency, and their environmentally friendly character.

Nevertheless, even if it has probably the longest history, heterogeneous catalysis, which is the most commonly used among all the catalytic tools (the other ones being homogeneous and enzymatic), still suffers from many drawbacks. Sometimes it is not selective enough, which increases evolution of products involved in green house effects (like CO_2, NO_x or particles), sometimes it requires high temperatures which is energy demanding, sometimes its lifetime is too short which is not economical, sometimes its regeneration procedures are difficult if not impossible.

Some of the reasons for these drawbacks are inherent to the "heterogeneous" character. The multiplicity of active sites in terms of surface and bulk structure and their low concentration prevent the easiness of achievement of a reliable structure-activity relationship, a necessary step for improvement of existing catalysts or even for a predictive approach for new catalytic reactions. Despite all these drawbacks, heterogeneous catalysis remains the most applied solution for one simple reason: catalyst separation from reagents or reaction products is usually easy which renders industrial processes more easily achievable.

A predictive approach to the design of heterogeneous catalysts is now slowly emerging due to the spectacular progresses made recently in the synthesis of new and structurally well defined materials. The nano-control of active sites via a pluridisciplinary approach is one of the ways to address this issue of predictive performances of catalysts. It is now possible to achieve the rational design and synthesis of well defined supports with the expected structure, acidity, porosity or shape in the field of oxides, or zeolites, carbon based materials or even of plurimetallic particles of given size, shape and composition. But the synthesis of

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materials, which are more and more defined from the atomic level to the nano level and finally to the centimetric level, is often not enough to warranty the required catalytic activity, selectivity, and lifetime. These new materials are most of the time a support of the metallic active site.

It is one of the reasons why the field of *"surface organometallic chemistry"* has been developed. This field concerns the grafting of organometallic or coordination compounds onto a reactive surface. By surfaces we mean those of simple oxides (from mesoporous materials up to zeolitic materials), those of metals (from unsupported nanoparticles to supported ones, up to single crystals), those of carbon (from carbon black to naphtenes to carbon nanotubes), those of carbides, nitrides, etc. Probably the surfaces of oxides are the most commonly used. The grafting of organometallic compounds onto these oxides aims at the synthesis of "single site" catalysts. In principle the detailed knowledge of the surface organometallic chemistry, that is the structure and chemical behaviour of the active site which results from a careful structural determination, leads to elucidation of elementary steps of heterogeneous catalysis and a structure-activity relationship can be achieved in several cases. Therefore a new generation of catalysts, controlling new and selective catalytic reactions and relevant improvements of existing catalysts, have been discovered on these materials. Such knowledge of the catalytic materials greatly benefited from the precision with which in situ and ex situ methods of structural and chemical characterization coming from advanced surface science and molecular chemistry may be carried out on such single sites (in situ IR, in situ ^{1}H, ^{13}C NMR, 2D NMR, EXAFS, Surface Microanalysis, determination of the stoichiometry of surface reactions, molecular models of the surface sites).

This book wants to analyze many aspects of this *"modern catalytic and surface chemistry by design"*. The reaction with surfaces of metal oxides or some specific silicates of *"organometallic compounds"* has been extended to *"coordination compounds"*. The types of metals cover not only *"transition metals with a variety of d^n electronic configurations"*, but also *"lanthanides and actinides"* or *"non transition metals"*. The types of surfaces have been extended to those of *"supported or unsupported metals or metal nanoparticles"*. Metallic nanoparticles of given size and composition, prepared by their *"synthesis in mesoporous materials"* or *"on simple oxides by carbonyl decomposition"*, have been broadly covered. The concept of metallic *single site* has been extended to *"building block approaches"* and *"immobilisation of homogeneous catalysts"*. A *"broad range of catalytic reactions"* such as those related to *"energy, raw materials and environment"* but also those involving more sophisticated aspects such as *"hydrosylilation and enantioselective reactions"* have been extensively covered. We have shown in this book how the molecular approach to silica-supported organometallic chemistry through the synthesis and investigation of *"silsesquioxanes based organometallic molecules"* is the basis of good models of the behaviour and structure of organometallic single sites on oxides but is also the origin of a family of catalysts on their own. The facile and selective *"Surface-mediated organometallic syntheses"* in particular of metal carbonyl clusters, a domain of intense research which results directly from surface organometallic chemistry, has been fully described.

We thank the authors for their excellent efforts and their willingness to mould their contributions to our conception of the book.

Jean Marie Basset
Rinaldo Psaro
Dominique Roberto
Renato Ugo

List of Contributors

Robert J. Angelici
Iowa State University
Ames Laboratory (U.S.-DOE) and
Department of Chemistry
Ames, IA 50011-3111
USA

Reiner Anwander
Universität Tübingen
Institut für Anorganische Chemie
Auf der Morgenstelle 18
72076 Tübingen
Germany

Craig E. Barnes
University of Tennessee
Department of Chemistry
552 Buehler Hall
Knoxville, TN 37996-1600
USA

Jean-Marie Basset
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Anne Baudouin
Laboratoire de Chimie Organométallique
de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

François Bayard
Laboratoire de Chimie Organométallique
de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Regina Buffon
University of Campinas
Institute of Chemistry–UNICAMP
PO Box 6154
13084-971 Campinas SP
Brazil

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Dominique Roberto, and Renato Ugo

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Jean-Pierre Candy
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Elena Cariati
Università di Milano
Dipartimento di Chimica
Inorganica
Metallorganica e Analitica
"Lamberto Malatesta"
via G. Venezian 21
20133 Milano
Italy

Mónica Laura Casella
Universidad Nacional de La Plata
and CONICET
Centro de Investigación y
Desarrollo en Ciencias Aplicadas
"Dr. Jorge J. Ronco" (CINDECA)
Facultad de Ciencias Exactas
47 N° 257
1900 La Plata
Argentina

Christophe Copéret
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Claudia Dragonetti
Università di Milano
Dipartimento di Chimica Inorganica
Metallorganica e Analitica "Lamberto
Malatesta"
via G. Venezian 21
20133 Milano
Italy

Osmar Alberto Ferretti
Universidad Nacional de La Plata and
CONICET
Centro de Investigación y Desarrollo en
Ciencias Aplicadas "Dr. Jorge J. Ronco"
(CINDECA)
Facultad de Ciencias Exactas
47 N° 257
1900 La Plata
Argentina

Atsushi Fukuoka
Hokkaido University
Catalysis Research Center
Sapporo 061
Japan

Gregory Godard
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Narcís Homs
Universitat de Barcelona
Departament de Química Inorgànica
Facultat de Química and Institut de
Nanociència i Nanotecnologia
C/Martí i Franquès 1-11
08028 Barcelona
Spain

Masaru Ichikawa
Hokkaido University
Catalysis Research Center
Sapporo 061
Japan
and
Tokyo University of Agriculture
Nodai Research Institute
Tokyo 156
Japan

Yasuhiro Iwasawa
The University of Tokyo
Department of Chemistry
Graduate School of Science
Hongo
Bunkyo-ku
Tokyo 113-0033
Japan

Philippe Kalck
Université de Toulouse
Laboratoire de Chimie de
Coordination du CNRS – UPR 8241
Composante ENSIACET-INPT
118, route de Narbonne
31077 Toulouse Cedex 4
France

Ireneusz Kownacki
Adam Mickiewicz University
Faculty of Chemistry
Grunwaldzka 6
60-780 Poznan
Poland

Emile Kuntz
Laboratoire de Chimie
Organométallique de Surface
C2P2 – UMR 5265 CNRS – CPE
Lyon – UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Emmanuel Lamouroux
Université de Toulouse
Laboratoire de Chimie de Coordination
du CNRS – UPR 8241
Composante ENSIACET-INPT
118, route de Narbonne
31077 Toulouse Cedex 4
France

Mihaela Lazar
National Institute for Research and
Development of Isotopic and Molecular
Technologies
65-103 Donath Street
400293 Cluj Napoca
Romania

Frédéric Lefebvre
Laboratoire de Chimie Organométallique
de Surface
C2P2 – UMR 5265 CNRS – CPE
Lyon – UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Christine Lucas
Laboratoire de Chimie Organométallique
de Surface
C2P2 – UMR 5265 CNRS – CPE
Lyon – UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Elena Lucenti
UdR dell'INSTM di Milano
via G. Venezian 21
20133 Milano
Italy

Aimery De Mallmann
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Bogdan Marciniec
Adam Mickiewicz University
Faculty of Chemistry
Grunwaldzka 6
60-780 Poznan
Poland

Thomas Maschmeyer
The University of Sydney
Laboratory of Advanced Catalysis
for Sustainability
School of Chemistry–F11
Sydney, NSW 2006
Australia

Anthony F. Masters
The University of Sydney
Laboratory of Advanced Catalysis
for Sustainability
School of Chemistry–F11
Sydney, NSW 2006
Australia

Sébastien Norsic
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Katrin Pelzer
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Pilar Ramírez de la Piscina
Universitat de Barcelona
Departament de Química Inorgànica
Facultat de Química and Institut de
Nanociència i Nanotecnologia
C/Martí i Franquès 1-11
08028 Barcelona
Spain

Marek J. Potrzebowski
Polish Academy of Sciences
Laboratory for Analysis of Organic
Compounds and Polymers
Centre of Molecular and
Macromolecular Studies
Sienkiewicza 112
90-363 Lodz
Poland

Elsje Alessandra Quadrelli
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Roberto Rinaldi
Laboratório Nacional de Luz
Síncrotron
Rua Giuseppe Máximo Scolfaro
10000
Barão Geraldo
13084-971 Campinas SP
Brazil

Dominique Roberto
Università di Milano
Dipartimento di Chimica
Inorganica
Metallorganica e Analitica
"Lamberto Malatesta"
via G. Venezian 21
20133 Milano
Italy

Erwan Le Roux
Department of Chemistry
Universitetet i Bergen
Allégaten 41
5007 Bergen
Norway

Catherine Santini
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Philippe Serp
Université de Toulouse
Laboratoire de Chimie de
Coordination du CNRS–UPR 8241
Composante ENSIACET-INPT
118, route de Narbonne
31077 Toulouse Cedex 4
France

Daravong Soulivong
Laboratoire de Chimie Organométallique
de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

François Stoffelbach
Laboratoire de Chimie Organométallique
de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Karol Szubert
Adam Mickiewicz University
Faculty of Chemistry
Grunwaldzka 6
60-780 Poznan
Poland

Mizuki Tada
Institute for Molecular Science
38 Nishigo-Naka
Myodaiji
Okazaki 444-8585
Japan

Mostafa Taoufik
Laboratoire de Chimie Organométallique
de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Chloé Thieuleux
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Jean Thivolle-Cazat
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Renato Ugo
Università di Milano
Dipartimento di Chimica
Inorganica
Metallorganica e Analitica
"Lamberto Malatesta"
via G. Venezian 21
20133 Milano
Italy

Laurent Veyre
Laboratoire de Chimie
Organométallique de Surface
C2P2–UMR 5265 CNRS–CPE
Lyon–UCBL
Bâtiment 308F
43, Blvd. du 11 Novembre 1918
69616 Villeurbanne Cedex
France

Antony J. Ward
The University of Sydney
Laboratory of Advanced Catalysis for
Sustainability
School of Chemistry–F11
Sydney, NSW 2006
Australia

Contents

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