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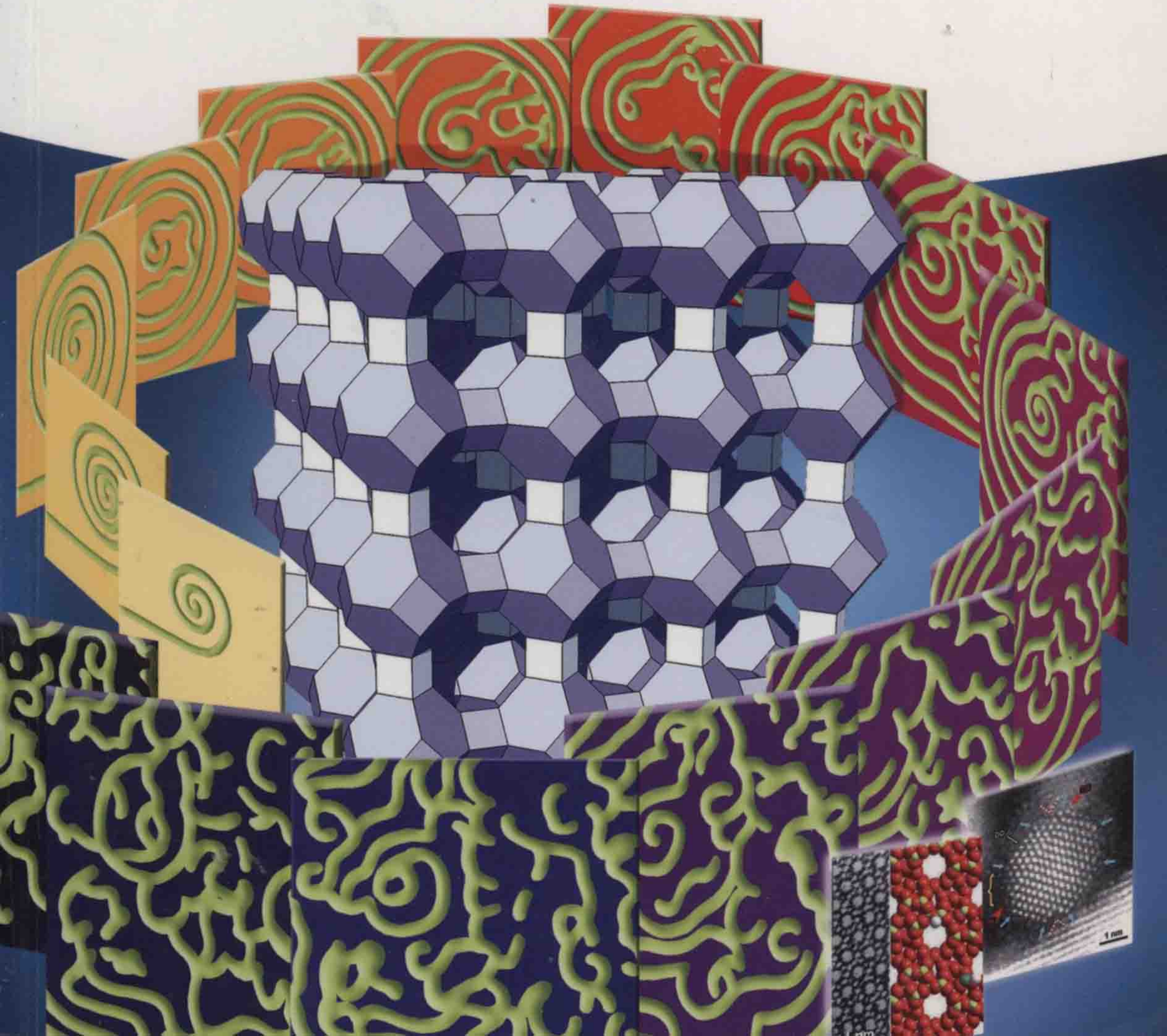
J. M. Thomas and W. J. Thomas

Principles and Practice of Heterogeneous Catalysis

Second, Completely Revised Edition



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Second, Revised Edition

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书 章

WILEY-VCH
Verlag GmbH & Co. KGaA

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

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Print ISBN: 978-3-527-31458-4
ePDF ISBN: 978-3-527-68380-2
ePub ISBN: 978-3-527-68378-9
Mobi ISBN: 978-3-527-68379-6

Cover-Design Adam-Design, Weinheim, Germany
Typesetting Laserwords Private Limited, Chennai, India
Printing and Binding Markono Print Media Pte Ltd., Singapore

Printed on acid-free paper

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Preface

It is a truth universally acknowledged that, in all segments of experimental science, it is easier to produce new knowledge than to interpret, rationalize and construct theories pertaining to that which has already been acquired. The pace at which the corpus of catalysis expands is very different from that of more somnolent topics of intellectual enquiry, such as Roman economic history or the etymology of arcane ancient languages. These thoughts have occupied our minds in preparing this second edition. Our aims in this edition remain unchanged: we direct our treatment both at senior students at university and the practicing researcher and industrialist. Whilst we delve into much hard factual information, we have endeavoured throughout to be illustrative rather than comprehensive concentrating whenever appropriate on basic principles. Chapter 3, however, dealing with the characterization of both industrial solid catalysts and model ones is of a rather comprehensive nature.

Seventeen years have now elapsed since the first edition appeared; and never has the need for new catalysts – and the related need for a strategy capable of their effective design – been greater than they are at present.

There is an exigent need to seek new ways of not only powering the planet in a sustainable manner, but also of finding new routes to produce the chemicals required for the maintenance of civilized life, and to do so using wherever possible renewable feedstocks. Even those scientists whose interest in catalysis has hitherto been rather slender are nowadays fully aware that clean technology and green chemistry and new sustainable methods of generating energy each call for processes that generate little or no waste, that utilize sustainable feedstocks, that avoid the use of noxious, toxic, potentially explosive or otherwise hazardous reagents and that operate under mild and environmentally benign conditions (preferably without use of non-aqueous or any other solvent). These 'onlookers', as well as the cognoscenti, know that industrial catalysis in general, and heterogeneous catalysts in particular (because they facilitate separation of products from reactants and make recycling, with it conservation of expensive or precious metals and ligands easy), hold the key to transforming attitudes and practices so as to pave the way towards a sustainable world (in the production of energy and commodities) in harmony with nature.

From the viewpoint of the academic scientist, catalysis also serves as a nexus that brings together numerous disciplines, each with its own identity: surface and solid-state chemistry, solid-state physics, organic and biochemistry, materials science and engineering, chemical engineering and robotics, crystallography, organometallic and theoretical (including computational) chemistry. As a consequence, catalysis is a topic conducive of cross-disciplinary activity and debate.

One of us (JMT), beginning 20 or so years ago, but especially during the past decade, has been preoccupied with some of the key issues that are of central importance in the pursuit of practices that will secure an environmentally better future through the agency of heterogeneous catalysis. To particularize, he has sought and found ways to oxyfunctionalize plentifully available hydrocarbons (present in oil or certain plant sources) so as to generate valuable products by using air or oxygen as oxidants (in the presence of appropriately designed solid catalysts) rather than employing aggressive (stoichiometric) materials such as CrO_3, $Na_2Cr_2O_7$, CrO_2Cl_2 and $KMnO_4$, which still figure as part of the portfolio of reagents currently utilized on laboratory scale by legions of organic chemists, but which are increasingly frowned upon by legislators and members of the general public when they perceive that some industrial processes still use these and other aggressive reagents.

In '*Setting the Scene*' (Chapter 1), an outline of some major new features introduced to this edition is given with reference also to some key advances made since the early 1990s. Those readers who veer towards chemical engineering will not be surprised to see some prominence given to membrane reactors, process intensification, new generations of auto-exhaust catalyst, fuel cells, lab-on-chip microreactors, multifunctional reactors and continously-operated non-isothermal reactors. The academic reader likewise will encounter discussions on nanocatalysis (especially the catalytic performance of nano-particles and nanoclusters of gold, as well as bimetallic clusters of up to 20 or so constituent atoms), on chiral (enantioselective) catalytic conversions at solid surfaces, on combinatiorial and high-throughput testing, and on the needs for solid catalysts to harness solar energy. Whilst it is illusory to imagine that one may soon (or ever) arrive at one all-embracing theory of heterogeneous catalysis – in the sense that we have a theory of electromagnetism, or of gravity or evolution – much needs to be done (and we have attempted it) to illuminate several dark theoretical and related corners of the subject. Great strides in the development and application of density functional theory (DFT) have been taken in the past decade, especially in the way that 'scaling laws' elucidate trends among existing catalysts and lead to predictions concerning the performance of new ones for relatively simple, but industrially important reactions such as Fisher-Tropsch conversion of CO and H_2 to hydrocarbons, the syntheses of ammonia and methanol, the water-gas shift-reaction and the methanation of CO.

An important new feature in this book, reflected by the emphasis given in the later chapters is the emergence of a strategy for the *de novo* design of Single-Site Heterogeneous Catalysts. Hitherto practitioners and theorists in the field of catalysis have not been able to devise a generally applicable way of assembling new heterogeneous catalysts, capable of facilitating the sweep of conversions embracing regio-selective, shape-selective and enantioselective processes. It is not enough to interpret the behaviour of existing catalysts, however subtle, refined or sophisticated the techniques, arguments and theories may be. It is essential to be able to arrive at new catalysts that, for example, may effect selective oxidations and reductions, and that can serve as new (environmentally benign) ways of producing heavy chemicals (e.g. adipic acid, terephthalic acid and caprolactam), builder molecules (e.g. epoxides, oximes, lactones and aldehydes), fine chemicals, polymers and even vitamins. These new catalysts must satisfy the demands of either the industrially-orientated or laboratory scientist, and at the same time meet ever-more stringent environmental legislative restrictions. Abatement of emissions from automobiles is a well-known phenomenon. It is less widely known that wood stoves are also a significant source of CO, SO_x and carbonaceous particulates. (There are 45 million residential wood-burning appliances in the US alone!) Many bulk chemicals, however, are still produced using renewable (*e.g.* petrochemical) sources. These factors are the subject of an extra chapter (Chapter 9) which extends the topics and examples that constitute Chapter 8.

Late in the 1980s one of us (JMT) felt that open-structure, nanoporous inorganic solids offered opportunities for the design of heterogeneous catalysts that could contain accessible, spatially well-separated and structurally well-defined active centres that simulate the behaviour of homogeneous and (to a lesser degree) enzymatic catalysts, as many zeolitic catalysts do. By the mid-1990s it became routinely possible to prepare high-area silicas with pore diameters controllably adjustable in the range of about 20–400Å. Because the inner walls of such siliceous nanoporous solids could be readily functionalized, this opened up the possibility of preparing an enormous variety of new heterogeneous catalysts that have well-defined single sites, just as in their homogeneous and enzymatic analogues. It transpires that there is now an enormously large family of metal-organic frameworks (MOFs), which are hybrid nanoporous solids with infinite network structures built from organic bridging ligands and inorganic connection centres. Many of these MOFs have novel microporous structure and robust thermal stability (see P A Wright, *'Microporous Framework Solids'*, RSC Publishing, **2008,** Cambridge, and Furukawa, Cordova, O'Keeffe and Yaghi, *Science,* **2013,** 341, 123044) and several of them can be produced as chiral crystals that exhibit novel enantioselectivity – see Ma, Lin *et al. Nature* Chemistry, 2010, 2, 838 and Ding, *Pure and Appl. Chem,* **2005,** 77, 1251. As a result of the major advances made in solid-state and preparative inorganic chemistry, it is now possible to prepare large numbers of thermally stable and otherwise robust nanoporous solids that act, as it were, as firm but flexible templates teeming with carefully fashioned, well-defined, accessible catalytically active centres. In a word, we now have the confluence of homogeneous and heterogeneous catalysts. It has long been possible to design powerful homogeneous catalyst – by controlling, *via* ligand manipulation – the electronic density at, and the stereochemical environment of, transition-metal ions. In a similar fashion, as is described elsewhere in this and other texts, heterogeneous catalysts of very many different kinds may now be rationally designed. (See KP de Jong (Ed) '*Synthesis of Solid Catalysts*', Wiley-VCH, **2009,** and JM Thomas '*Design and Applications of Single-Site Heterogeneous Catalysts: Contributions to Green Chemistry, Clean Technology and Sustainability*', Imperial College Press, **2012**).

In preparing this monograph, we have been fortunate to have conferred on a multiplicity of topics with experts from far and wide. Individuals and research groups throughout the world have entered into discussions with us, and we wish to express our gratitude to them. We are particularly thankful to Professor Lynn Gladden, CBE, FRS, FREng for her input to the sections on reactor design and cognate topics and to Professor KSW Sing for his input to Chapter 4. One of us (JMT) is especially indebted to the other (WJT), who, despite fighting a losing battle against total blindness, has manitained his buoyant optimism and good cheer. He is also deeply indebted to Professor Kenneth Harris (Cardiff) for the constancy of his help and advice, and to Rowan Leary for his willing help on numerous occasions. Mrs Rebecca Pritchard deserves special thanks for her cheerful approach to the vast reams of typing that she has undertaken. JMT is particularly grateful to Dr Waltraud Würst of Wiley-VCH for her expert editorial help.

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