Exteriors Exposed

Advances in Catalysis. Vol. 45. Achievements, Failures and Prospects During Fifty Years of "Advances in Catalysis". By *Bruce C. Gates* and *Helmut Knözinger.* Academic Press, San Diego 2000. 448 pp., hardocover $150.00.—ISBN 0-12-007845-7

Writing from these Laboratories, fifty two years ago, my predecessor but three, Sir Eric Rideal along with V. I. Komarewsky and W. G. Frankenburg, co-founders and co-editors of Vol. 1 of the series *Advances in Catalysis and Related Subjects*, asserted that "…in spite of (some) amazing practical successes of catalytic methods, and our increasing knowledge of biocatalysis, only modest progress has been made in the scientific elucidation of the working mechanism and of the basic nature of catalytic action. As a consequence, a purely empirical approach is still the only safe way to search for efficient catalysts whenever the problem arises of carrying out a desirable and thermodynamically possible chemical transformation with the help of specific catalysts".

"The main reason for this situation seems to be that a full understanding of catalytic action would require, for any given case, a much deeper knowledge of the nature and action of atomic and molecular forces than we possess today. In addition, in the field of heterogeneous catalysis the fine structure of solid surfaces plays a decisive role, and much more would have to be known about the qualitative and quantitative nature of solid surfaces than we know at present. In other words, a science of catalysis has to be erected on foundations which still have to be laid".

In the course of the intervening years the foundations of the science of catalysis can legitimately be claimed to have been laid with the almost bewildering variety of techniques now available for the elucidation, in atomic detail, of solid surfaces. Equally, there are some well-known textbook examples of catalytic reactions that occur at metal surfaces, where the precise sequence of events that ensue from the impact and adsorption of reactants to the desorption and escape of products is known in great detail. Indeed Chapter 1 (by Ertl) of this volume gives just such information, especially in regard to the oxidation of carbon monoxide by oxygen in the presence of single-crystal metal surfaces. Proceeding from the microscopic (i.e., quantum and atomic) level through the mesoscopic to the macroscopic levels of spatial dimension, Ertl discloses many striking facts. Thus, when this simple oxidation proceeds on a platinum (111) surface it transpires that the assumptions underlying the time-honoured Langmuir–Hinshelwood framework are not fulfilled. At the conclusion of his 70 page scholarly discourse Ertl cites the philosophy propounded by Langmuir in 1922 when he said: "…let us confine our attention to reactions on plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies".

But Ertl's view is that, notwithstanding the substantial progress that has been made, "the actual situation is far more complex and still offers demanding challenges for future research".

Langmuir's advice ("…confine our attention to plane surfaces…") has certainly been taken to heart by five of the six remaining authors who have contributed to this worthy volume: King et al (on adsorption energetics and bonding); Somorjai and McCrea (on sum-frequency generation for probing surface vibrational spectroscopic changes accompanying catalytic reactions at metal single-crystal surfaces); Wintterlin (on scanning tunneling microscopic studies of catalytic reactions); Nørskov and Hammer (on theoretical surface science and catalysis via theoretical insights, concepts and calcularions); and Freund et al, who provide a number of illuminating answers to the question posed by the subtitle of their chapter (What do we learn from studies of oxide-supported cluster model systems?). Only in the chapter by Barteau and Idriss is there extensive discussion of the phenomenology of high-area (oxide) catalysts—the porous materials to which Langmuir alluded nearly eight decades ago. These authors focus on active sites on oxide catalysts with special reference to dehydration, coupling, and reductions of a variety of organic reactants. They also make a bold attempt to underline the connections between metal oxide, single-crystal surface, and high surface area catalysts, all in the cause of future catalyst design.

Insofar as covering the fundamentals of surface science as it affects catalysis is concerned, this volume is an unqualified success. Gates and Knözinger in their Preface, echoing Rideal, state that "Catalysis provided much of the driving force for the early development of surface science". This is still true, even to the extent that many investigators who set out optimistically to unravel the mysteries of heterogeneous catalysis find satisfaction in the study of surface structure (or of adsorption, migration, and desorption) alone.

It is an undeniable fact that surface science continues to shore up the foundation of catalytic science. But the sceptic would argue that, technically brilliant as the contributions to surface physics and surface chemistry have been

during the past half century, there are precious few examples which one might cite where a full-blooded study of the fundamentals of surface science have spawned altogether new solid catalysts. It still remains true that an approach that integrates and extends accumulated chemical experience and knowledge (both qualitative and theoretical) is as viable as it ever was in the emergence of new or improved catalysts. It is relevant to quote the words of the late Charles Kemball, a pioneer in this area, who in 1970 stated: "I would add here a plea to those who are fascinated by ultrahigh vacua and work with single crystals to remember that there is a danger they may become imprisoned in their own ivory towers".

Notwithstanding these reservations, the contributors to this volume—without exception, all heavyweight performers on the world stage—have produced admirably lucid chapters, the one by Nørskov and Hammer being among the best available, synoptic accounts of the use of density functional theory to describe reactions at surfaces. This is the first time ever for editors of "*Advances*" to focus exclusively on a single theme. It is to be hoped that they will repeat the practice frequently in future. There are many candidate themes: shining new biocatalysts, including newly arrived methods of directed Darwinian evolution,[1, 2] and chemically modified mutant enzymes[3] is one; and of older vintage, but still pregnant with opportunity—and here I must declare an interest—the impact of solid-state chemistry on catalysis is another. We do not any more rely, as Rideal's contemporaries did fifty years ago, on a purely empirical approach.

[1] M. T. Reetz, *Angew. Chem.* **2001**, *40*, 292; *Angew. Chem. Int. Ed.* **2001**, *40*, 284.
[2] F. H. Arnold, *Nature* **2001**, *409*, 253.
[3] J. B. Jones and G. de Santis, *Acc. Chem. Res.* **1999**, *32*, 99.

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Silicon-Containing Polymers. The Science and Technology of their Synthesis and Applications. Edited by *Richard G. Jones, Wataru Ando* and *Julian Chojnowski.* Kluwer Academic Publishers, London 2000. 768 pp., hardcover $ 315.00.—ISBN 0-412-83110-4

The long expected monograph edited by R. G. Jones, W. Ando, and J. Chojnowski is finally available from Kluwer Academic Publishers! On almost 800 pages, it presents the latest developments (up to 1999) in an area which is of extreme interest to chemical industry. The topics are treated in 28 review articles which are divided into four general subjects: "Polysiloxanes", "Polycarbosilanes and Polysilazanes", "Polysilanes and Related Polymers", and "Special Topics".

All the contributions have been written by internationally recognized authors or by the pioneers of the fields themselves. Therefore, it is a delight to read this book, which gives detailed and reliable information about a surprisingly diverse variety of interesting recent developments. The synthesis of polysiloxanes is extensively discussed, including directed synthesis of new polymers, copolymers, elastomers, interpenetrating networks, polysilsesquioxanes, and modified surfaces. All the chapters include a list of important review articles together with recent references. This strategy allows a compact presentation and rapid access to important information.

Polycarbosilanes, polysilazanes, and polysilanes already find applications at the present time, for example, as preceramics, in xerography, or in direct lithography. Polysilanes are also considered as materials for light emitting diodes (LEDs). Several contributions from leading industrial laboratories provide interesting examples of the current state of the art of development. Other important branches of research discussed are methods for inducing chirality (e.g., in helical polymers) and materials with linear and nonlinear optical properties, complex superstructures and topography (e.g., dendrimers, meso- and nanostructures, sol–gel processes, silicates with a defined porosity), and the tuning of orbital energies and band gaps (solids). By combining new physical methods (such as controlled injection of charge carriers into polymers, or time-of-flight spectroscopy of charge carriers) with sophisticated synthetic methods it is possible to design entirely new devices for microelectronics. A report on liquid crystalline polymers is another highlight in the multitude of applications. The book concludes with chapters on plasma processing of silicon-containing monomers and (dry) sub-γ-lithographic applications of silicon polymers in microelectronics.

In summary, the articles in *Silicon-Containing Polymers* present a degree of scientific interdisciplinarity and broadness of subject matter rarely found elsewhere. However, there is a growing interest in "smart" silicon-containing materials in areas such as nanotechnology, biocompatible materials, or materials for microelectronics. Also, many of the recent achievements are likely to influence or to be transferred to the chemistry of carbon polymers. Therefore, it was important to document the current state of the art in this field of research. The book now provides fast access to information for scientists entering this rapidly expanding area.

The contributions are mainly written from the point of view of the synthetic chemist, but doors to other disciplines such as physical chemistry, solid-state physics, and to applications are wide open. This makes the monograph especially interesting and valuable. *Silicon-Containing Polymers* is not just an attractively presented summary of current scientific vanities, but rather a systematic report on the overall state of research in the area. The presentation may sometimes be too dense and detailed for a textbook, but is excellently suited as a source of information for graduate students and research scientists. The book is almost free of misprints and errors, and has a useful alphabetical index. The work undoubtedly sets new standards, making it an essential acquisition for every scientific library. *Silicon-Containing Polymers* is not only a "must" for

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research groups active in silicon polymer chemistry and silicon solid-state chemistry but is also highly recommended to any scientist interested in materials science as an interdisciplinary, mind-opening field of study.

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Candid Science. Conversations with Famous Chemists. By *István Hargittai*. Imperial College Press, London 2000. xii+516 pp., paperback £ 25.00.—ISBN 1-86094-228-8

Since 1995 Springer Verlag has published the journal *The Chemical Intelligencer*, which was founded by István Hargittai, and is devoted to the "culture" of chemistry, in other words its history, philosophy, and interaction with other sciences. A journal with that as its declared aim can be expected to strike out beyond the boundaries of chemistry and to invite dialogue with widely different disciplines, not only with the natural sciences. Biographical articles have played an important role in the journal from its beginning. This book collects together (in a slightly altered and extended form) the conversations that the author and his wife Magdolna had with some 40 chemists over the last few years, and which originally appeared in *The Chemical Intelligencer* (an "intelligencer" is a bringer of news or a scout reporting on a reconnaissance). As Hargittai's journal is only taken by a few libraries, and probably entirely unknown to many chemists, the collection of these conversations in a single volume is very useful. As expected, it contains interviews with many of the "usual suspects" (L. Pauling, C. Djerassi, V. Prelog, E. Chargaff, D. Barton, M. Dewar, R. Hoffmann, G. Olah, J. Roberts, and others), for whom there already exists much biographical or autobiographical material, sometimes quite extensive. Readers who are already familiar with the blue volumes of the ACS series *Profiles, Pathways, and Dreams*, edited by Jeff Seeman, will not find much here about those well-known names that is new. However, as well as those eminent chemists, many of them Nobel prize-winners, the Hargittais have also talked with some scientists whose names are not (permanently) in the limelight, but who have nevertheless made groundbreaking contributions. There are interesting conversations touching on fullerene research, the only area for which there is a group of interconnected interviews, not only with H. Kroto, R. Smalley, and R. Curl, but also with W. Krätschmer, E. Osawa, R. Whetten, E. Gal'pern, and I. Stankevich, the last two giving some relief from the otherwise rather narrow concentration on Western Europe and the USA. Some other subjects from outside the western world are N. Semenov and A. Ulubelen, the latter an example of the (too few) women interviewed.

So what are the conversations about? Mostly they are purely biographical—origins and family background, early influences on the choice of profession, review of scientific and academic career, the politics of university life and research, self-evaluation of the subject's contributions to chemistry, etc. This all makes very interesting reading, but for a book with the title *Candid Science* (the original word from the Latin means sincere or honest), it is not enough. The interviewers should have been "harder" in their questioning, with the aim of getting deeper insights into the personalities of creative individuals. For example, there could be questions concerned with why many scientists attach such great importance to making a name for themselves, with the social behavior of scientists, or with how they react to competition, jealousy, or resentment. Occasionally, for example when scientists were questioned about individuality and unorthodoxy, as touched on in the conversations with Chargaff, Djerassi, Dewar, P. Scheuer, and A. Zewail, one sees the beginnings of where and in what ways the book might have gone further in the presentation of scientists' lives. Instead of developing the usual themes for the well-known chemists in the form of a constant succession of questions and replies, it would have been better to summarize their careers briefly (and in smaller type), leaving space for a more in-depth treatment to follow.

Briefly: the book offers a collection of widely varied and tasty hors d'oeuvres, but only rarely do these provide food for thought that could lead on into a full menu.

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Calixarenes in Action. Edited by *Luigi Mandolini* and *Rocco Ungaro*. Imperial College Press, London 2000. 271 pp., hardcover £ 35.00.—ISBN 1-86094-194-X

Chemical Abstracts Services will tell you that in 1989, the year C. David Gutsche's highly regarded *Calixarenes* was published, 63 articles relating to those cyclic phenol derivatives could be found in the literature. Ten years of growth later (at 34 % per year), a similar search digs up a total of 450 "hits" for 1999. Apparently then, there is no sign whatsoever that the supramolecular field is losing interest in these fascinating molecules. And indeed why should there be such a decline? In the push to move calixarene chemistry from the fundamental realm to its place in the developing "megatrend" that is nanotechnology, a lot of groundwork still needs to be done. We are some way from routinely building nanoscale molecular species or materials with distinct physicochemical properties that are a function of (the nano) scale. Be that as it may, a cursory glance at some of the total of 3219 calixarene "hits" from *CAS* throws up numerous signs of the exciting possibilities that nanotechnology may offer. One of those more recent "hits", a new book dedicated to calixarenes (and the odd resorcinarene), gives us some indication of how far we have come, or if you are so inclined, how far we have yet to go. *Calixarenes in Action*, a compendium of the thousand and one things you can do with these molecules, is the latest addition to the small but growing list of reference books dedicated to the subject. As the title implies, it focuses on the often unique physical and chemical properties of calixarene-based structures. Thus it nicely complements Gutsche's second book on the subject, *Calixarene Revisited*, in which the focus is primarily historic and synthetic.

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Working through each contributed chapter with a fine-toothed comb seems slightly redundant, since if you are reading these words it is a safe bet that you know what sort of chapters are included in the book. Just think supramolecular. Perhaps the only surprise (at least to this reviewer) that the table of contents throws up is the Eurocentricity of the book. Now don't get me wrong, the fact that a major proportion of calixarene research is carried out in Europe may have something to do with this fact, but there were a couple of moments when I felt that some contribution from, for example this (left) side of the pond, would have been helpful. This is especially so if you are one of the down-trodden minorities in the field, that is, a resorcinarene chemist. I will come back to this point later.

As far as calixarenes are concerned, the bulk of the "action" generally involves the attractive noncovalent forces that can work between identical (or at least nearly identical) molecules, in other words self-assembly, and the noncovalent forces at work between two (generally) dissimilar molecules, namely, host/guest properties. After a brief introductory chapter covering conformation and nomenclature, the book treats us to nine chapters dedicated to these two topics. Of those nine contributions, two focus on self-assembly with the formation of distinct molecular or supramolecular species, and the formation of essentially infinite systems (of the thin-film type), covered in separate chapters. In terms of host/guest chemistry, we first come across a review of molecular modeling of calixarene/guest complexes. Subsequently their host properties are divided up into the gas, solid, and solution phases, with the last of these subdivided into the binding of metal ion, quaternary ion, anion, and neutral species. Finally, the book finishes on a twist to the host/guest theme with a review of the development of catalytic systems, one facet of calixarene chemistry which is hard to scratch, but which will surely play a significant role in the future expansion of the field.

Any problems with the text? Well, there were a couple of times where typographical errors detracted from the read, and the odd moment when grammatical problems raised their ugly heads (but hey, you should see my Italian or Dutch or German). Also, as I alluded to previously, there were moments when I missed topics that would have fitted nicely into the text. Thus, to pick just one example from that down-trodden minority, Strongin's colorful sugar-binding resorcinarenes could definitely have fitted somewhere into the text. To be fair to the editors, these types of omissions may simply be due to that age-old problem of defining the boundary between calixarenes and resorcinarenes, and since this problem is unlikely ever to disappear, perhaps the best way around it is for someone to write a book dedicated to resorcinarenes. After all, a *CAS* search indicates that the resorcinarene/cavitand field is roughly the same size as the calixarene field was when Gutsche wrote *Calixarenes*. Maybe one of us down-trodden minorities has a job to do! Anyway, I digress. Overall, the text in question is a useful and natural extension to the calixarene books already in print, and with the above points in mind it should serve as a useful reference for the community at large, and for all the newcomers who will contribute to the continued expansion of the field.

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