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BOOK REVIEW

Catalysis by Metals and Alloys. (Studies in Surface Science and Catalysis, Volume 95). V. Ponec and G. C. Bond. Elsevier, Amsterdam/New York. 734 + x pp., $297.00.

Catalytic science covers a very broad range of catalyst types: of these, metallic catalysts of one sort or another form an extremely important group. This importance arose initially because such catalysts have been (and are) used in many industrially important applications, and because they have provided very useful models for the study of catalytic reaction mechanisms. With a literal explosion in the volume of published material having occurred over the last quarter-century or so, an in-depth review of catalysis by metallic catalysts is welcome. Both of the authors of the present volume are very well known for their research contributions on catalysis by heterogeneous metals and alloys, and the catalysis community owes them a substantial debt of gratitude for undertaking the enormous labor which must have been involved in the preparation of this unique book. We know of only one previous attempt since World War II at a general and broad review of heterogeneous metallic catalysis, "Catalysis by Metals," the very influential book by G. C. Bond (1962).

"Catalysis by Metals and Alloys" is quite a large book with a total of 729 pages of text and a total of 2319 numbered reference citations (some having more than one reference for a single reference number). Each of the chapters contains references at the end plus a prologue and an epilogue, an arrangement which is certainly the most convenient for the reader. Since any particular subject is usually heavily referenced, the reader without considerable prior knowledge will often be faced with a difficult reference selection problem, and this is probably made more difficult by an index which is fairly rudimentary (the subject index runs to only 5 pages or so). While this reference selection problem is, in a number of cases, greatly helped by leading references being highlighted in the text, this is not always done. The book is made up of 14 chapters plus a short (5-page) prologue and a short (5-page) epilogue. The prologue is essentially a summary of historical background, while the epilogue is a summary of what the authors consider to be the main issues which emerge. Both prologue and epilogue are rather whimsical expositions which, on the whole, do not do very much to enlighten the reader as to the authors' intentions or to indicate where the subject is currently heading.

The chapters are: Chapter 1, "Structure and Properties of Metals and Alloys"; Chapter 2, "Experimental Techniques of Solid State Physics Relevant to Research on Alloys"; Chapter 3, "The Electronic Structure of Alloys: Experimental Results"; Chapter 4, "Surface Composition of Alloys"; Chapter 5, "Physical Properties and Structure of Small Metal and Alloy Particles"; Chapter 6, "The Catalytic Cycle"; Chapter 7, "Preparation and Characterization of Metal and Alloy Catalysis"; Chapter 8, "Adsorption on Alloys"; Chapter 9, "Catalysis by Alloys—General Features"; Chapter 10, "Reactions of Hydrogen and Alkane-Deuterium Exchange"; Chapter 11, "Catalytic Hydrogenation and Dehydrogenation"; Chapter 12, "Oxidation Reactions"; Chapter 13, "Reactions of Alkanes and Reforming of Naphtha"; and Chapter 14, "Syngas Reactions."

The core consideration is the relationship between catalytic performance, particularly selectivity, and catalyst structure, particularly surface structure. To this end, rather more than 50% of the book deals with various aspects of the structure of metallic and alloy catalysts, including of course a detailed consideration of highly dispersed catalysts. We have no quarrel with this approach, because it is certainly true that the development and use of a wide range of physical techniques during the past two or three decades—well described in this book—have revolutionized our understanding of the details of catalyst structure, and thus have made it possible to seek correlations with the chemistry of catalyst performance in a manner that could not even have been contemplated previously. Nevertheless, despite the detail with which the book presents this material, there are some lapses or omissions which would have been better avoided. Thus, for instance, in the discussion related to alloy surface composition the possible effect of the ambient gas phase on the surface composition appears to be lacking. This is a nontrivial matter, since it is the surface composition of the working catalyst which is important, not the nominal composition as estimated under UHV conditions. In this respect, it is worth noting that describing a complex physical technique on paper is one thing: giving some idea of the practical pitfalls is quite another. It would, of course, be impossible to expect the authors to go for down this track for reasons of space. Yet, for instance, transmission electron microscopy is so filled with well-recognized problems when a reliable estimate of supported cluster size is required that a brief discussion about this point, or at least referencing, would have been expected.

The structure of the book contains some idiosyncratic features which would probably have been better avoided. Thus, for some obscure reason, Chapter 6, "The Catalytic Cycle," is interposed between two chapters which focus attention on catalyst structure rather than on catalytic processes as such. There is no apparent reason for this incongruity, and it may well be judged to interrupt the logical flow of the text.

In fact, the present Chapter 6, "The Catalytic Cycle," contains a great deal more than an account of the concept of the catalytic cycle and, for instance, contains major sections with headings: 6.3,"Methods of Investigating Catalysed Reactions"; 6.4, "Kinetics of Heterogeneously Catalysed Reactions"; 6.5, "Structure Sensitivity and Particle Size Effect"; and 6.6, "Catalytic Consequences of Metal–Support Interactions." All of these are important topics and easily earn their place. Nevertheless, setting to one side the question of the appropriateness of the title to Chapter 6, one needs to recognize some surprising omissions. For instance, although there is a subsection titled "Heat Transfer and Mass Transport Limitation" in Section 6.3, there is no mention of the effect that mass transport limitations have on the apparent activation energy and on the apparent reaction kinetics, while Section 6.4 has no comment about the significance of the rate-determining step in multistep processes, nor how to handle kinetics at energetically nonuniform surfaces. Section 6.5, "Structure Sensitivity and Particle Size Effects," although being a generally good exposition of a complex and rather confused subject, makes no mention of C_6-alkane isomerization on platinum as a well-known example. Of course, even in a large book one cannot expect the authors to cover everything in detail: however, at least referencing important matters would be better than nothing.

We do not believe it to be a reviewer's task to "proofread" a text with the object of providing a detailed and exhaustive list of faults—the "nit-picking" approach. It suffices to say that the chapters in this book dealing with various aspects of catalyst structure (Chapters 1–7) are informative, comprehensive, and well done, particularly in view of the size of the litera-

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ture. The chapters which deal with various aspects of the catalytic process (Chapters 6–14) are the ones about which we have rather more reservations. First we must say that these chapters nominally cover the catalytic processes reasonably comprehensively. However, by focusing so heavily on what they regard as their central theme—the relation between selectivity and catalyst structure—the authors have often downplayed the question of activity to an unreasonable extent. There are a number of omissions which we find disturbing. Thus, it has been known for a considerable time that highly dispersed platinum (~1 nm) generated in the channels of nonacidic L-zeolite has very high selectivity for the dehydrocyclization of *n*-hexane to benzene. Given that this is now a substantial industrial process, it is surprising that it is not mentioned in the book when particle size effects are being discussed.

We need to ask who should consult this impressive monograph of Ponec and Bond? We are reluctant to recommend this book to a beginner in the field or to a scientist working in a related field and anxious to learn about catalysis. The beginner might be discouraged from working in a field where, according to the authors, "all the old work should be done again!" While the critical, and sometimes supercritical, dissections of the authors are most commendable and stimulating to the specialist, it may give the uninitiated the impression that our level of knowledge is very low, while our quarrels are very loud. It is true that we are still struggling with the mechanism of all chemical reactions, including catalytic ones. But we now understand a lot about the principles of catalytic cycles, the way they turn over, and the preparation of active, selective, and durable catalysts.

As an example, consider ammonia synthesis. This catalytic process is one of the oldest, largest, and most economical in terms of catalyst cost and durability: the metallic iron-based catalyst is also the best understood of all, yet the authors' discussion of recent work on ammonia synthesis is limited to less than two pages, including two figures. Although it may well be but an isolated example of how problems accumulate, it is disconcerting to find that the treatment of this topic contains blemishes which certainly should not be there and which will certainly confuse most readers. Thus, in Fig. 26 (on p. 287) the upper curve, which shows the TOF (turnover frequency) vs iron particle size (d_{Fe}), should (by reference to the literature cited) carry the label N_{N_2}, not N_{H_2}. In fact, this label is relevant only to the data points to the left of the break in the upper curve and to one of the three points which appear to the right of this break in the original reference: for reasons which are not apparent, the authors have chosen to replace these three points (which occur as a cluster) with a single point in Fig. 26. In fact, Fig. 26 contains a collection of data points for which a variety of different symbols are used but not identified. Point identification in terms of catalyst and adsorbate, including the points in the cluster of three referred to above, requires use of the explanatory table which was included in the original reference but which the authors of this book have chosen to delete from Fig. 26. Furthermore, in transferring Fig. 26 from the original literature to the book, three nonexisting data points have been added, no doubt inadvertently: as shown in the figure, they are removed by orders of magnitude from the other experimental data (lower curve in Fig. 26) and, if taken seriously, would seem to discredit the work. In addition, by replacing the cluster of three identified data points relevant to the right-hand end of the upper curve in Fig. 26 (cf. the comments above), the authors have obliterated an important conclusion related to the active site identity. These three practically coincident data points establish, for this particular industrial catalyst, that when iron sites are counted with chemisorption of hydrogen, carbon monoxide, or nitrogen at high temperature, the turnover frequency for ammonia synthesis is about the same. Now, if it is agreed that H_2 and CO count all the iron sites exposed, while N_2 counts only the sites that are most active in the synthesis, it follows that this commercial catalyst exposes predominantly these most active sites, the C_7 sites discovered by others on model iron catalysts and on single crystals. Finally, in relation to Fig. 26, we believe that the appellation to the lower curve would have been better written as N_{H_2}, N_{CO} (as in the original reference) rather than $N_{H_2} + N_{CO}$, which may confuse some readers into thinking about a gas mixture. In their discussion of Fig. 26 the authors say that we are taught another "important lesson, one that may have wider significance," namely that "in hydrogenation and hydrogenolysis studies, *and quite generally* (our emphasis), the number of active sites is tacitly assumed to equate to the number of hydrogen atoms or carbon monoxide molecules adsorbed." In fact, we believe that an understanding of the significance of the details relating to active sites on iron catalysts for ammonia synthesis should lead all but the most imprudent reader to conclude that *in general* one ought *not* tacitly assume any such thing.

As would be expected in a book of this size, it is not difficult from a detailed examination to come up with a collection of points which can be disputed mainly as matters of opinion. It would be unnecessary, unfair, and tedious to enumerate these: we only draw attention to the following. In Chapter 7 ("Preparation and Characterization of Metal and Alloy Catalysts") the reader would have benefitted from some information about epitaxially grown metallic films and film structure in general, while a discussion of metallic "blacks" would have benefitted from some information about the problems of surface cleanliness and sintering. In Chapter 13 ("Reactions of Alkanes and Reforming of Naphtha") the chapter title is likely to induce in the reader false expectations as to its content, while the immediate precursor to C–C bond rupture shown as the $\alpha\beta$ species in Fig. 9 (on p. 599) might well be questioned on the grounds that the same species is involved in deuterium multiple exchange (cf. p. 467), implying that hydrogenolysis and deuterium multiple exchange should occur in about the same temperature range—which is not usually the case.

In another discussion, the authors exclaim *caveat lector*, or reader beware. This warning applies to their book as well. However, the *aware* reader will benefit enormously in reading this remarkable thesaurus of catalytic lore.

Finally, we add another warning: *caveat emptor*, or buyer beware. The nominal price of this book is U.S.$297.00 so, as a retail purchase, many will pay in excess of U.S.$300.00 after the addition of handling and shipping charges, etc. A book of this price would surely have warranted an author index.

The book is available from Elsevier Science, Publishers, P.O. Box 211, 1000 AE Amsterdam, The Netherlands; or from Elsevier Science Publishers, P.O. Box 945, Madison Square Station, New York, 10160-0757 (for U.S.A. or Canada); or from local distributors who handle Elsevier Science books.

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