Alloys in Catalysis

Catalysis by Metals and Alloys, Studies in Surface Science and Catalysis, Volume 95
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Catalysis impacts directly on all aspects of our daily life, whether it be enzymatic catalysis, integral to the existence of living things, or the more widely recognised synthetic catalysis of the laboratory, chemical plant or motor car. Even within synthetic catalysis there are numerous ways of categorising the body of known information. Thus, we talk of heterogeneous, homogeneous and acid base catalysis, to name but a few, each in itself being a major subject of academic and industrial study.

The phenomenon of heterogeneous catalysis was first noticed at the beginning of the nineteenth century. Amongst the early observations was that of Humphrey Davy, who in 1817 reported that coal gas laden air continued to generate heat on platinum wires after the flame beneath them had been extinguished. Further experimentation showed that this phenomenon only happened with platinum and palladium; copper, silver, gold and zinc were ineffectual (1). These observations created great interest, and over the next 20 years or so such luminaries as Faraday, Döbereiner and Berzelius, as well as Humphrey and Edmund Davy, contributed to this young science. To Berzelius is attributed the origin of the term "catalysis" for the observed phenomena (1). Since that time, of course, much work has been published on the subject. It is therefore not surprising that this book, which concerns itself primarily with catalysis by alloys (an alloy is defined as "any metallic system containing two or more components, irrespective of their intimacy of mixing or the precise manner in which their atoms are disposed") runs into 14 chapters, in excess of 700 pages, and references around 2000 published papers.

The first half of the book covers the chemistry and physics of alloys and alloy surfaces in some detail, starting in the first chapter with a review of the theoretical aspects of solids, in particular metals and alloys, and of chemisorption of atoms and molecules onto the surfaces of such materials. The next two chapters deal with a selection of the more important experimental techniques which have been used by solid state physicists and surface scientists to generate information on the nature and structure of catalysts, and of the chemisorbed species thereon. It seems to be the fate of many of these experimental techniques that they are generally known by acronyms, for example XPS, SIMS, EXAFS, AES, HREM; so I found it useful that each of these techniques was briefly explained at the beginning of the appropriate section!

These first three chapters are the underpinning of what is to follow. Thus, chapter four begins to look at the energetics and surface composition of alloys and discusses surface segregation, whereby the composition of the surface is different from the bulk composition, and how this surface segregation can be influenced by the presence of chemisorbed molecules and by particle size. The effects of surface segregation in small metal crystallites on a support, which is the most frequently used form for practical catalysis, may be different from those in larger metal particles for several reasons, and the former are often difficult to study by the spectroscopic techniques mentioned above. However, qualitatively, it is often very useful to be aware of the effects that occur with the larger particles, when attempting to understand the results obtained in catalytic reactions using these small supported metal crystallite systems. This chapter also provides some case histories of the battleground for understanding the performance of alloy systems between proponents of the rigid electronic band theory and what might be termed the "segregationalists". Alloys comprising one element from the nickel, palladium, platinum group with one from the copper, silver, gold group should differentiate between the two theories. Accordingly, much work has been done on these systems, and for many years the balance of data seemed sometimes to favour one, then the other. However, some of the data, even with sophisticated surface techniques, was subsequently shown to be flawed, and the rigid band theory is now not favoured.

The basic fundamentals of catalysis and catalytic reaction theory are the subject of chapter six, and this is followed by a major chapter on the preparation and characterisation of metal and alloy catalysts, together with no less than 465 references. This chapter reviews various techniques for preparing macroscopic materials (films, foils, wires, single crystals, etc.), small unsupported metallic particles (metal blacks, colloids, Raney alloys), and supported metal catalysts of many types, and constitutes a very useful source-book in its own right!

The second half of the book is devoted to the use of alloy catalysts in practical catalytic reactions, beginning with some general observations in which the authors very sensibly recognise that amongst all of the reasons for studying catalysis on alloy systems, the primary ones are the desire to learn more about how catalysis works, and the wish to produce catalysts having better performance. There is, rightly, a feedback loop from one to the other, but much of the work published in the literature stems from a more empirical approach. Of course, the majority of industrial catalysts comprise metals or alloys on an "inert" support: in practice such supports are rarely inert, and thus contribute in one way or another to the reactivity of the catalyst. Also, in many cases such catalysts are not properly characterised (and in some cases not characterised at all, except by reactivity), and so effects observed may not be directly attributable to the presence – or absence – of alloy formation.

The authors have chosen to formulate the chapters in this half of the book on the basis of reaction type. Thus, there are chapters on reactions involving hydrogen (including isotopes), hydrogenation/dehydrogenation, oxidation, reforming, etc. While this is probably the most practical approach – and the best from the point of view of the practising chemist – it inevitably means that references to individual alloy systems are spread throughout the text, although there are useful summaries of a few individual systems, such as the alloys of nickel, palladium, platinum with copper, silver, gold, referred to above.

Surprising is the very small amount of space devoted to pollution control catalysis – especially for motor vehicles – which has been a major practical use of catalysis for more than twenty years, and which almost invariably has involved multimetal catalysts.

But, I must not complain: this book surely represents several man-years of effort in accumulating the references and attempting to summarise them, and is a truly laudable effort. Professor Bond's first major book published almost 35 years ago (2) was a source of inspiration to a whole generation of catalyst chemists: hopefully this volume will provide an equal impetus to the further study of alloys.

Readers will be pleased to note that a number of citations appearing in "Catalysis by Metals and Alloys" are to articles which have appeared in *Platinum Metals Review*.

This book is available from Elsevier, P.O. Box 211, 1000 AE Amsterdam, The Netherlands, or in the U.S.A. and Canada from Elsevier Science Inc., P.O. Box 945, Madison Square Station, New York, NY 10160-0757. D.E.W.

References

1 D. McDonald and L.B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982, Chapter 12
2 G. C. Bond, "Catalysis by Metals", Academic Press, London, 1962

Platinum Group Metals Conference

Over 200 offers of contributions have already been received for presentation at the Sixth International Conference on the Chemistry of the Platinum Group Metals, to be held at the University of York from 21st to 26th July, 1996. A second circular and application form will be available shortly. Anyone wishing to contribute or attend should contact Dr John F. Gibson, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, U.K., Fax: 0171-734-1227, Email: conferences@rsc.org.