

An Important Work of Reference

Chemistry of the Platinum Group Metals: Recent Developments

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The declared aim of this very readable and welcome volume is to cover recent developments in the chemistry of the platinum group metals. The variety of treatments and styles used depends partly on the subject matter of each chapter, partly on when the area of technology was last reviewed and partly on the particular interests and expertise of each individual author. The result is a collection of chapters in a variety of styles, but each is useful and interesting, in its own way.

The opening chapter is by Professor F. R. Hartley of the Cranfield Institute of Technology, Bedford, U.K., and considers the occurrence, extraction, properties and uses of the platinum group metals. The dominant producers of the platinum group metals are South Africa, the U.S.S.R. and, to a lesser extent, Canada. The route for conversion of the South African ore into final concentrate is indicated, as are the classical separation and more recently developed solvent extraction methods for dividing the concentrate into the six individual metals. The physical and chemical properties of the six metals are described. Therefore the principal applications of the platinum group metals depend on either their nobility or their catalytic properties.

At first sight nobility and catalytic activity might seem unlikely properties to be exhibited by the same element, but their nobility depends on the large number of valence *d*-electrons which are available for tight cohesive bonding. These same valence shell *d*-electrons provide orbitals having characteristics which match those of a range of simple substrates such as hydrogen, carbon monoxide and unsaturated hydrocarbons, and thus promote their reactivity. The predominant uses of platinum are in autocatalysts and jewellery, while palladium finds application principally in the electrical and dental areas, uses of ruthenium are mainly

in the electronics and electrochemical areas, and the market for rhodium is strongly led by its requirement in autocatalysts.

Catalytic Activity

The general introduction to catalysis by the platinum group metals, written by G. C. Bond of Brunel University, U.K., puts the subject into good historical perspective and draws most of its exemplification from the heterogeneous field, although the common factors present in homogeneous, heterogeneous and enzymic catalysis are indicated. The analytical techniques available for structure determinations of chemisorbed layers are described, and there are sections on catalyst poisons, metallic catalysts and supported metal catalysts. The various types of useful reactor configurations are considered, as are the kinetics and reactor modelling aspects. Important industrial applications of the platinum group metals catalysts include ammonia oxidation, power station and automobile emission control, petroleum reforming, and catalytic hydrogenation in fine chemicals manufacture.

Benefits of Catalytic Combustion

The chapter on catalytic combustion by D. L. Trimm of the University of New South Wales, Australia, describes an extension of pollution control technology, using the heat produced, preferably with the minimum production of unwanted pollutants. The design requirements for catalytic heaters are discussed, with indications that the combustion efficiency depends on the material used to support the platinum or platinum/palladium catalyst, on fuel flow rate, the type of fuel used and oxygen diffusion from the ambient atmosphere. Therefore the use of catalytic combustion in gas turbines can reduce the temperature of gas phase free radical reactions to below 1650°C,

thus reducing nitrogen oxide emissions by an order of magnitude.

Synthesis Gas Chemistry

The chapter on the use of platinum group metals catalysis in the synthesis of chemicals from syngas by G. R. Steinmetz and Z. R. Zoeller of Eastman Chemical Company, Tennessee, U.S.A., indicates that the dramatic rise in crude oil prices in the early 1970s gave a corresponding surge in the quest for alternative carbon sources. This need followed the significant developments in organometallic chemistry and the result was an explosive growth in the use of organometallic catalysts (particularly homogeneous systems) for the generation of chemicals from synthesis gas. The platinum group metals have played an integral part in these developments and several processes have either been commercialised or are under consideration; these include the Monsanto process for the rhodium-catalysed carbonylation of methanol to acetic acid, and the Tennessee Eastman and Halcon SD rhodium-catalysed carbonylation of methyl acetate in the presence of hydrogen and dimethyl ether to yield acetic anhydride. Rhodium based catalyst systems are also used in the Johnson Matthey/Union Carbide/Davy McKee hydroformylation process for the conversion of olefins (for example propylene) to aldehydes. One common feature of these three rhodium-based processes is that most or all of the oxygen component is retained. Current economics dictate that a new process must possess both high selectivities and a high overall yield.

There is some overlap of the content of the syngas chapter with that written by A. W. Parkins of King's College, London, on recent developments in platinum group metal catalysts in the chemical industry, but both heterogeneous and homogeneous processes are considered here, and the growing interdependence of these two areas of catalysis is recognised. This chapter deals with both major and minor processes of interest to industry, including the rhodium-catalysed reactions indicated above, the vapour phase

palladium-catalysed route to vinyl acetate, the Wacker process for the palladium-catalysed production of acetaldehyde from ethene, supported palladium catalysts for the hydrogenation of unsaturated hydrocarbons, and platinum catalysed hydrosilylation reactions. Fischer-Tropsch reactions for the synthesis of higher hydrocarbons and other chemicals from methane and syngas, based on ruthenium catalyst systems, are described by Steinmetz and Zoeller and by Parkins. The Texaco molten salt process for the conversion of syngas to alcohols/esters in tetrabutylphosphonium iodide (m.p. 96°C) in the presence of ruthenium carbonyl is also described, together with a number of other reactions with industrial potential.

Catalysis in Molten Salts

The chapter by J. F. Knifton of Texaco Chemical Company, Austin, Texas, U.S.A., on platinum group catalysis in molten salts is a valuable review of the wide range of chemical reactions now studied in this type of medium, which should be considered in parallel with homogeneous and heterogeneous catalysis in the methodology of both laboratory and commercial scale operations. In addition to the alcohol synthesis mentioned above, this technique has been used for the direct synthesis of ethylene glycol (ruthenium-rhodium catalyst or ruthenium alone), or ethene and propene (ruthenium-cobalt) from syngas.

C-H Bond Activation

The review of C-H bond activation by J. R. Chipperfield of the University of Hull, U.K., covers this important area of work as far as the recent developments in homogeneous catalysis are concerned. The homogeneous systems are dealt with in the context of the heterogeneous industrial processes concerned with dehydrogenation, cracking and partial oxidation.

Oxidation Chemistry

The comprehensive chapter on oxidation by E. S. Gore of Johnson Matthey, New Jersey, U.S.A., gives an historical introduction,

indicating that the first example of catalysis by a metal was reported by Sir Humphry Davy in 1817 who described the oxidation of inflammable gases over platinum. The declared purpose of this chapter is to review the present state of platinum group metals catalysed homogeneous oxidations with the emphasis on reactions of synthetic and industrial potential and on recent developments since 1980. Even so, the chapter has four hundred references and covers a wide spectrum of organic chemical transformations, including the reactions of aliphatic and aromatic hydrocarbons, alcohols, ethers, sulphides and amines. Although platinum is well established for use in commercial heterogeneous catalytic processes, it was not until 1962 that the use of a platinum group metal (palladium) in an industrial homogeneous catalytic process was first reported, this being in the Wacker process for the conversion of ethene into acetaldehyde.

Electro- and Photochemistry

A chapter indicating the importance of platinum group carbonyls in developing the potential of catalytic processing is written by J. A. Davies and C. T. Eagle of the University of Toledo, Ohio and Williams College, Massachusetts, U.S.A., respectively. The principal sections in this chapter are on photo- and electrochemistry and reduction reactions. The use of light to generate thermally active catalysts has led to the catalytic synthesis of functionalised compounds from arenes and alkanes under exceptionally mild conditions. Through an understanding of fundamental electrode processes, it may prove possible to design solution phase systems or modified electrodes capable of exerting a significant electrocatalytic effect on the reduction of carbon dioxide, an alternative to hydrocarbons as a major initial source of carbon. Platinum group carbonyls have begun to show promise as catalysts for a number of novel reduction reactions which have potential for future developments, including the reduction of nitrogen oxides by carbon monoxide.

In the chapter on electrochemical applica-

tions by E. N. Balko of the Engelhard Corporation, New Jersey, U.S.A., the area considered is platinum group metals coated anodes in which the requirements for industrial anodes are listed and then the anodic characteristics of platinum, iridium and ruthenium and their oxides are considered in some detail. At least 80 per cent of the chlorine production in the western world is now manufactured on ruthenised titanium. This review is primarily concerned with several of the most widely used platinum group metals coatings in their common industrial applications, that is oxygen and chlorine discharge.

An authoritative chapter on the role of platinum group metals in the photodecomposition of water, written by A. Mills of the University College of Swansea, U.K., includes both homogeneous and heterogeneous systems and indicates the relevance of this approach to the conversion of solar energy into chemical energy.

At the present state of knowledge, the heterogeneous systems are considered to be more durable. Homogeneous catalysts for either hydrogen or oxygen evolution will require substantial further development before they are likely to offer a serious alternative to their heterogeneous counterparts, such as colloidal platinum or powdered hydrated ruthenium(IV)oxide, respectively.

Homogeneous Catalysis by Palladium and Platinum Systems

The contribution by G. K. Anderson of the University of Missouri, U.S.A., is on the organometallic and homogeneous catalytic chemistry of palladium and platinum and is very substantial with over four hundred references, in spite of its focus being on work carried out only in the past ten years. Both the organometallic aspects of the topic and the use of these species in catalytic reactions are described.

Soluble palladium catalyst systems have been widely applied in organic chemical synthesis using, for example, carbonylation reactions; both platinum and palladium systems have

featured in catalytic hydrogenation, hydroformylation and hydrosilylation reactions.

Iridium and Rhodium Systems

Another very substantial review, with over five hundred references, has been contributed by F. H. Jardine of the North East London Polytechnic, U.K. The organometallic and homogeneous catalytic chemistries of rhodium and iridium are described, including hydrogenation and dehydrogenation reactions, hydroformylation, hydrosilylation and carbonylation and decarbonylation. In general, only recent work is covered but a special feature is made of rhodium(II)carboxylate catalysed cyclisations involving alpha-diazo esters or ketones, a topic which has been overlooked in previous reviews.

The chapter by W. Levason of the University of Southampton, U.K., on the chemistry of the platinum metals in high oxidation states brings up to date a topic frequently reviewed in the past. The text is in a highly summarised form and is a very useful reference work for inorganic chemists working in this area. For halides, oxides and the related anions, there is sufficient resemblance between the chemistries of the six elements to allow the topics to be treated together. For the co-ordination chemistries with neutral ligands, however, the differences currently seem large enough for them to be treated separately. There are 443 references in this chapter and it also includes an addendum covering the 1989 literature, whereas the main text covers principally the years 1981 to 1988.

Activity with Biologically Important Molecules

Amino acid and peptide complexes are reviewed by H. Kozłowski and L. D. Pettit of the University of Wrocław, Poland and the University of Leeds, U.K., respectively. Interest in the interaction of platinum metals with biologically important molecules was stimulated some twenty years ago with the discovery by Barnett Rosenberg and colleagues at Michigan State University, that certain

platinum complexes exhibit anti-cancer activity. Intensive research to explain the chemistry and biochemistry of platinum complexes which behave as cytotoxic agents and to produce effective and less toxic anti-cancer drugs has led to huge projects based on the chemistry of platinum complexes with many biologically active ligands, including amino acids and peptides. Amino acid complexes of the platinum group metals are also of interest as catalysts and, as such, have been the subject of several recent studies; this may become a rewarding field for research, although it is made difficult by the kinetic inertness of many of the complexes formed and the complicated aquo-chemistry of the metal ions themselves.

A review of cancer chemotherapy involving platinum and other platinum group complexes has been written by C. A. McAuliffe, H. L. Sharma and N. D. Tinker of the University of Manchester Institute of Science and Technology, U.K. The parent of this class of platinum drugs is "cisplatin" and this is widely used for the successful treatment of ovarian and testicular cancers and, to a lesser extent, head and neck tumours. A very significant research effort on the synthesis and evaluation of candidate platinum compounds for new drug formulations has now led to the introduction of the second generation drug "carboplatin" which produces less severe side effects in patients.

Electronic Applications

The final chapter in this wide ranging book is written by P. D. Gurney and R. J. Seymour of Johnson Matthey Technology Centre, Reading, U.K., and indicates the many uses for the platinum group metals in electronics. Platinum finds most of its applications in the thin film area but palladium and ruthenium are predominant in the formulation of thick film conductor and resistor systems. In fact, 51 per cent of the demands for palladium and ruthenium in the western world are in the electrical/electronics area. A wide variety of platinum group metal compounds have been used to deposit thin metal films via chemical vapour decomposition techniques, while physical vapour deposition

involves the production of a metal film via sputtering or evaporation at low pressure. Platinum silicide, made by the sputtering of a thin platinum film onto a silicon surface, finds application in bipolar integrated circuits and in Complementary Metal Oxide Semiconductor (CMOS) structures. Amongst other topics discussed in this chapter are platinum group metal alloys for liquid metal ion sources (LMIS) and the use of platinum group metals in magnetic data storage media, thin-film magneto resistive sensors, magneto-optic media, and gas sensors. Ruthenium oxide finds wide application in thick film resistors, and palladium-silver systems are the basis of the most widely used thick film conductors as well as being valuable components in multilayer ceramic capacitors.

The use of platinum group metals is helping in the development of the new high temperature superconducting systems; they are being used in the formation of barrier layers for thin films of these materials. Platinum group metals complexes have also been incorporated into semiconductors, and into one-dimensional

conductors where the columnar structures result in the compound having highly anisotropic properties.

Overall, this book reviews progress in the development of knowledge on the chemistry of the platinum group metals in the areas where there have been significant technological advances during the last ten years. There are good links throughout between scientific investigation and its commercial application, although one very important application area, that is automotive emission control catalysts, only receives brief comments, and there is no discussion of the platinum fuel cell catalyst systems which are currently receiving significant attention in both research and commercial development. The book provides a useful and stimulating reference work, particularly as it covers many different fields of scientific research in the same volume and it should therefore appeal to a wide range of research workers, particularly those interested in developing new areas of platinum metals research or commercial applications in a synergistic manner.

D.T.T.

Efficient Ruthenium Dye-Sensitised Solar Cell

To-date, a large scale use of photovoltaic devices for electricity generation has not developed because the available technology is prohibitively expensive. However, a recent letter from the Swiss Federal Institute of Technology describes a photovoltaic cell system for which a commercially realistic energy conversion efficiency is claimed (B. O'Regan and M. Grätzel, *Nature*, 1991, 353, (6346), 737). Colourless, optically transparent films of titanium dioxide, displaying the fundamental absorption edge of anatase (band gap 3.2 eV) are deposited on conducting glass sheet. These 10 μm films, which consist of particles with an average size of 15 nm and a particle surface roughness factor of 780, gave linear photo-current response up to full sunlight.

The subsequent deposition of a monolayer of the trimeric ruthenium complex dye $\text{RuL}_2(\mu\text{-(CN)Ru(CN)L}'_2)_2$ (where L is 2,2'-bipyridine-4,4'-dicarboxylic acid and L' is 2,2'-bipyridine) onto the titania results in a deep brownish red coloration of the film. The high surface area of the semiconductor film and

the ideal spectral characteristics of the dye lead to a high proportion of the incident solar energy flux being harvested in a cell employing this system in the photoanode; the counter electrode consisting of conducting glass coated with a few monolayers of platinum. The very fast electron injection observed with dyes such as this tri-ruthenium complex, combined with their high chemical stability, makes these compounds look attractive for practical development.

Exceptionally high efficiencies for the conversion of incident photons to electrical current are claimed, with the device harvesting 46 per cent of the incident solar energy flux. The overall light to electric energy conversion yield is 7.1 to 7.9 per cent in a simulated solar light and 12 per cent in diffuse daylight. With current densities greater than 12 mA/cm^2 and with at least five million turnovers being achieved without decomposition, practical applications may be feasible. The technology described thus seems to represent a significant advance in photovoltaic cell technology.

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