

International Congress on Catalysis

THE PLATINUM METALS FIND WIDE APPLICATION

The 9th International Congress on Catalysis (9th ICC) held in Calgary, Alberta, Canada during the week commencing 27 June 1988, was the latest in the series of congresses started at Philadelphia in 1956. Sadly, this meeting also marked the death of Prof. R. B. Anderson, who had contributed much to the understanding of catalysis as well as being co-chairman of the 9th ICC organising committee.

Almost 100 lectures and 170 posters were presented by authors from over 30 countries during the five day meeting, which was attended by some 850 delegates. The theme of "Catalysis: Theory to Practice" attracted contributions from academic and industrial workers, especially from the chemical process industries. Environmental issues were not overlooked despite the surprisingly low number of papers addressing pollution control technology, and much was made of the need to minimise industrial pollution by the use of suitable processing techniques.

Many of the papers were concerned with the catalytic properties of the platinum group metals, and it is clear that the interaction between the noble metals and the catalyst support or promoters is attracting much attention. In particular, catalytic sites have been identified at the interface between noble metal particles and neighbouring oxide species, or associated with platinum group metal compounds such as sulphides, mixed oxides, silicides and borides. The use of EXAFS as a structural technique now appears to be almost routine. With such a wide ranging meeting, it would be difficult to include all the papers in this review, so the authors apologise for any omissions. The first four volumes of proceedings of the 9th International Congress on Catalysis have been edited by M. J. Phillips and M. Ternan, and published by the Chemical Institute of Canada (1785 Alta Vista Drive, Suite 300, Ottawa, Ontario, K1G 3Y5, Canada). Volume V, contain-

ing the plenary lectures and discussion, will be published shortly.

Synthesis Gas Conversion

Platinum group metal catalysts are well known for their ability to convert synthesis gas. Prof. A. T. Bell, of the University of California, gave a plenary lecture reviewing the current understanding of the Fischer-Tropsch reaction to form hydrocarbons. A number of techniques including infrared, reactive scavenging and radio-tracers showed that the rate determining step is dissociative adsorption of carbon monoxide, which is enhanced by co-adsorbed hydrogen. The carbon atoms are then hydrogenated giving a pool of reactive, adsorbed hydrocarbon intermediates. C. A. Mims, L. E. McCandlish and M. T. Melchior (Exxon Research and Engineering Company, U.S.A.) speculated that this may include C₂ species. A single crystal study by F. M. Hoffman and J. L. Robbins (Exxon Corporate Laboratories, U.S.A.) suggests that co-adsorbed hydrogen promotes carbon monoxide dissociation by removing oxygen atoms from the surface, thus preventing recombination of carbon and oxygen atoms. G. A. Melson and E. B. Zuckerman, of the Virginia Commonwealth University, compared bifunctional ruthenium/zeolite catalysts with conventional ruthenium/alumina catalysts. Impregnation of the zeolite ZSM-5 with triruthenium dodecacarbonyl deposited ruthenium only on the external surface of the support particles. Examination of the product distribution showed that the zeolite supported catalyst had greater selectivity to aromatic and low molecular weight hydrocarbons. L. Petrakis, M. Springel-Huet, T. Ito (CNRS, France) and T. R. Hughes, I. Y. Chan and J. Fraissard (Chevron Research Co., U.S.A.) studied platinum dispersion in zeolites using a ¹²⁹Xe NMR signal seen only from Pt-Xe interaction inside the cages.

The selectivity of rhodium-containing catalysts for conversion of syngas to oxygenates attracted much debate, especially concerning the distinction between promoters which increase the rate of carbon monoxide dissociation and those which influence chain length and oxygenate selectivities. Several groups had studied the structure of bimetallic catalysts containing a transition metal and a noble metal. J. W. Niemantsverdriet, S. P. A. Louwers, J. van Grondelle, A. M. van der Kraan, F. W. H. Kampers and D. C. Koningsberger (Eindhoven University, Netherlands) suggest that their FeIr/silica catalysts for methanol synthesis contained ferric ions in addition to an iridium-iron alloy. M. Ichikawa, A. Fukusha and T. Kimura (Hokkaido University, Japan) achieved a similar structure when bimetallic Group VII/iron/silica catalysts were prepared using mixed metal carbonyl clusters, for example Rh₄Fe, instead of the chlorides and nitrates used by the Dutch group. The role of the rhodium precursor (chloride and nitrate) was also studied by B. J. Kip and E. G. F. Hermans (Eindhoven University) and R. Prins (ETH Zurich, Switzerland), who concluded that differences in metal particle morphology were more important than residual anions on the support. A dual site mechanism was proposed by N. A. Bhole, C. Sudhakar, K. B. Bischoff, W. H. Manogue and G. A. Mills of Delaware University for oxygenate synthesis using rhodium/molybdenum/alumina; rhodium activated the carbon monoxide which was then hydrogenated by hydrogen atoms migrating from pentavalent molybdenum sites which had dissociated the molecular hydrogen.

Synthesis gas processes using platinum group metals catalysts which have been commercialised are mainly homogeneous reactions. H. Bach, W. Gick, W. Konkol and E. Wiebus, of Ruhrchemie A.G., West Germany, described a recent development in the hydroformylation of alkenes to aldehydes; the new Ruhrchemie-Rhône Poulenc process uses a homogeneous rhodium catalyst rendered water soluble by its sulphonated phosphine ligands. Other papers on homogeneous processes included a kinetic

study on the direct formation of ethylene glycol from synthesis gas using ruthenium and rhodium complexes by T. Deguchi, M. Tamura, M. Ishino and S. Nakamura (Sumitomo Chemical Co., Japan) and the production of formamides and amines using ruthenium melt catalysts by J. F. Knifton, D. C. Alexander and E. E. McEntire (Texaco Chemical Co., U.S.A.).

Hydrotreating and Hydrogenation

Prof. H. Knözinger of the University of München, West Germany, reviewed current hydrodesulphurisation (HDS) catalysis technology, then indicated the growing interest in hydrodenitrogenation (HDN). Although commercial HDS catalysts are predominantly sulphided base metals (CoMo and NiMo), there is interest in platinum group metals especially for HDN. J. M. van der Eijk, H. A. Colijn and J. A. R. van Veen (Shell-KSLA, Netherlands) had compared Group VIII metals with sulphided catalysts for the HDN of quinoline and reported significant differences in behaviour; ruthenium and rhodium were very active but also promoted C-C hydrogenolysis; whereas platinum, palladium and iridium had lower HDN activity but better selectivity. The hydrogenation of biphenyl using a nickel-ruthenium mixed sulphide had been studied by M. Vrinat, M. Lacroix and M. Breyse (CNRS, France) and A. Bellaloui, L. Mosoni and M. Roubin (Univ. Claude Bernard, France); pure NiS₂ converted to inactive Ni₃S₂ in the reactor, whereas mixed sulphides with more than 17 atomic per cent ruthenium retained an active pyrite structure. The high activity of the pyrite structure of RuS₂ was also noted by Y. J. Kuo and B. J. Tatarchuk of Auburn University, U.S.A., during thiophene HDS. Sulphidation temperature and H₂S : H₂ ratio were believed to affect the surface structure with respect to S-S and M-S bond formation.

The roles of metal edge and face catalytic sites during liquid phase hydrogenation of a probe molecule, (+)-apopinene, using palladium/silica and platinum/silica catalysts were reported by G. V. Smith, D. Ostgard and

T. Nishizawa of Southern Illinois University, U.S.A., and F. Notheisz, A. G. Zsigmond and M. Bartok (Jozsef Attila Univ., Hungary). Incremental poisoning by CS₂ provided evidence that hydrogen dissociation and rapid π -allyl isomerisation occurred on edge sites, whereas face sites accounted for addition and slow isomerisation. The role of adsorbate chemisorption strength and hydrogen surface coverage was used by J. Massardier, J. C. Bertolini and A. Renouprez (CNRS, France) to explain the difference in activity and selectivity between different palladium single crystal faces and palladium/silica for the hydrogenation of butadiene. A comparison between several Group VIII metal catalysts for deuterium exchange with hydrocarbons was given by R. Brown, C. Kemball and I. H. Sadler (University of Edinburgh, U.K.).

A multi-step process using a promoted platinum/silica catalyst was described by M. Rusek (CIBA GEIGY, Switzerland) for the n-alkylation of anilines. This appeared to be a bifunctional catalyst, making use of the hydrogenation activity of the platinum and the acid-base properties of the support which were readily modified by the addition of alkaline earth ions. D. Richard, P. Fouilloux and P. Gallezot (CNRS, France) had studied the liquid phase hydrogenation of cinnamaldehyde using platinum/carbon catalysts. Charge transfer to the platinum particles, either from steps in the graphitic surface or from iron promoter atoms, improved the selectivity to cinnamyl alcohol. Iron also played an additional role by activating the C=O bond.

The effect of support and catalyst pretreatment on hydrogenolysis catalysts was discussed by several authors. G. C. Bond and R. R. Rajaram (Brunel University, U.K.) and R. Burch (University of Reading) had investigated ruthenium catalysts supported by titania, alumina and silica. Contamination of ruthenium/titania by chloride seemed to inhibit hydrogen spillover onto the support. Residual chloride was also examined by H. Miura, H. Hondou, K. Sugiyama, T. Matsuda and R. D. Gonzalez (Saitama University, Japan), who

supported the view of the previous authors concerning the partition of chloride between metal and support. They estimated that an ensemble of 4 to 5 ruthenium atoms was required for propane hydrogenolysis. Particle morphology was another factor influencing catalyst performance; according to E. J. Braunschweig, A. D. Logan, S. Chakraborti and A. K. Datye of the University of New Mexico, different oxidation and reduction procedures caused changes in the metal morphology of rhodium/silica catalysts.

Bimetallic Catalysts

Bimetallic catalysts often exhibit activities and selectivities for hydrogenation or hydrogenolysis of hydrocarbons that are dramatically different from those of their monometallic counterparts. A. J. den Hartog, M. Holderbusch, E. Rappel and V. Ponec (University of Leiden, Netherlands) have studied alloys of iridium with either copper or gold and argue that mixed iridium/copper ensembles are present. The effect of pretreatment on the surface composition of platinum-ruthenium/silica catalysts was discussed by M. Asomoza, G. del Angel, R. Gomez, E. Rejai and R. D. Gonzales of the University of Illinois; surface segregation of platinum was favoured by vacuum drying, although air drying reduced the subsequent reduction temperature. A. J. Hong, B. J. McHugh, L. Bonneviot, D. E. Resasco, R. S. Weber and G. L. Haller (Yale University) proposed that copper could form either 2-dimensional layers or 3-dimensional islands on the surface of ruthenium supported on different grades of silica. These differences in morphology had a profound effect on the performance of the catalyst.

The beneficial effect of the addition of a second metal, for example rhenium, tin or germanium, to platinum/alumina reforming catalyst is well established. Temperature programmed techniques and XPS were used by J. N. Beltramini (University of Queensland) and D. L. Trimm (University of New South Wales) to show that reduced germanium improves the activity of the catalyst, whereas unreduced germanium oxide promotes coking.

Similar effects with platinum-tin/alumina were reported by A. Sachdev and J. Swank of the University of Michigan; divalent tin was present and promoted hydrogen mobility.

Pollution Control and Poison Resistance

The poison resistance of platinum group metals can often be enhanced by the physical properties of the support. S. Nishiyama, T. Yoshida, Y. Nishikawa, S. Tsuruya and M. Masai (Kobe University, Japan) applied a thin coating of silica to platinum/alumina catalysts and found no deactivation due to deposition of organo-nickel or organo-vanadium during hydrogenolysis of n-hexane. A metal-support interaction was discussed by M. Guenin, P. N. da Silva, J. Massardier and R. Frety (CNRS, France) as a means of weakening metal-sulphur bonds and so improving the thiotolerance of iridium/magnesia and iridium/silica-alumina catalysts.

The reactions of carbon monoxide with oxygen and nitric oxide over noble metal catalysts are important for the catalytic control of automotive exhaust emissions. Addition of molybdena and ceria to rhodium/silica catalysts for the reduction of nitric oxide by carbon monoxide was described by W. C. Hecker, M. D. Wardinsky, P. C. Clemmer and R. B. Breneham (Brigham Young University, U.S.A.), who found that ceria increased the rhodium dispersion, whereas molybdenum decreased it. The activities of the rhodium and rhodium-molybdenum catalysts were comparable, but the catalysts differed in terms of rate order with respect to carbon monoxide and nitric oxide. C. H. F. Peden, P. J. Berlowitz and D. W. Goodman (Sandia National Laboratories, U.S.A.) reported carbon monoxide oxidation kinetics on rhodium(III) single crystals. Under highly oxidising conditions, the near surface region became oxidised (possibly to Rh_2O_3) and the decomposition of carbonate-like intermediates became rate-limiting. Rhodium(III) was also used by G. B. Fisher, S. H. Oh, C. L. DiMaggio and S. J. Schmeig (General Motors Research Laboratory, U.S.A.), and D. W.

Goodman and C. H. F. Peden (Sandia National Laboratories) to study the inhibition of carbon monoxide oxidation by nitric oxide. They suggest that the dissociation of nitric oxide at moderate temperatures leads to inhibition of oxygen adsorption by high coverages of nitrogen atoms. Another paper, by F. C. M. J. M. van Delft, K. Siera, R. J. Vreeberg and M. J. Koster van Groos (University of Leiden), and A. D. van Langeveld and B. E. Nieuwenhuys (Eindhoven University) examined the effect of the surface structure of platinum-rhodium alloys on the adsorption of nitric oxide dissociation, which appeared to be faster on rhodium-rich surfaces, especially those with higher index crystallographic planes.

Carbonyl Clusters and Unusual Compounds

A plenary lecture on catalysts derived from carbonyl clusters was given by Prof. L. Guzzi of the Hungarian Academy of Sciences. A number of authors had used carbonyl clusters to prepare catalysts but there were contributions which specifically examined the behaviour of the cluster during preparation and use. In particular, cluster integrity, modes of decomposition and the role of the cluster-support interaction in inhibiting nucleation were discussed. S. D. Jackson and G. Owen (ICI, U.K.), and R. B. Moyes, M. S. Roberts, C. G. Scott, P. B. Wells and P. Worthington (University of Hull) described the conversion of hexameric osmium clusters to stable dimers when supported on a cadmium sulphide support. H. H. Lamb, T. R. Krauss and B. C. Gates (University of Delaware) also had used osmium clusters but stressed the importance of anion formation on basic supports such as magnesias. EXAFS had been used by F. B. M. Van Zon, G. Visser and D. C. Koningsberger (Eindhoven University) to identify flat metal particles when a tetrairidium dodecacarbonyl cluster was supported on alumina. They suggested that the metal-support interaction involved long O-Ir bonds, possibly as an Ir-(OH) interaction. Another study using EXAFS examined the genesis of platinum particles

formed by impregnation using chloroplatinic acid. F. Le Normand, D. Bazin, H. Dexpert and P. Lagarde (Univ. de Paris Sud, France) and J. P. Bournonville (IFP, France) obtained Pt-Pt, Pt-Cl and Pt-O bond lengths using EXAFS every 15 minutes during slow isothermal decomposition/reduction of the catalyst precursor.

The Wacker process normally uses aqueous palladium dichloride to convert alkenes to aldehydes. The palladium is reduced to the metal but this is immediately reoxidised using a Cu(I)/Cu(II) couple which in turn is reoxidised by air. E. van der Heide, M. de Wind, A. W. Gerritsen and J. J. F. Scholten (Delft University, Netherlands) described a stable, heterogenised Wacker catalyst which operated in the same manner as the homogeneous catalyst system except that the Cu(I)/Cu(II) couple was replaced by a monolayer of vanadia applied to either alumina, titania or zirconia. Another example of a heterogenised, homogeneous catalyst used a monomeric palladium complex coordinated to the interlayer support of an aminated lithium hectorite. S. Shimazu, T. Ishada and T. Uematsu of Chiba University, Japan, claimed that the intercalated palladium catalysts showed higher activity and selectivity than the unsupported palladium complex for the liquid phase hydrogenation of isoprene. S. B. Ziemecki (DuPont, U.S.A.) used palladium to enhance the redox properties of phosphorus-vanadium-molybdenum heteropolyacids.

Two papers from the Polish Academy of Sciences concerned the catalytic properties of

palladium compounds. Work by W. Juszczyk, Z. Karpinski, J. Pielaszek, I. Ratajczykowa and Z. Stanasiuk on the reaction between neopentene and hydrogen suggested that high temperature reduction of palladium/silica led to the formation of palladium silicide, which was less active than pure palladium but more selective toward isomerisation. Palladium black catalysts prepared by borohydride reduction are known to contain boron; W. Palczewska, M. Cretti-Bujnowska, J. Pielaszek, J. Sobczak and J. Stachurski described the effects of segregation of boron to the surface under the influence of various pretreatments. Enrichment of the surface with palladium boride was found to increase the stereoselectivity during the hydrogenation of acetylenic groups.

Concluding Remarks

This was a fascinating meeting. Platinum group metals are used in a wide range of catalysts from platinum bimetallics for reforming petroleum products to carbon-supported systems for the synthesis of fine chemicals and drugs; and platinum metal technology is contributing significantly to the prevention of further deterioration of the environment. Already widely used, it is clear that in future years the platinum group metals can increase the role that they play in catalysis. The high interest in platinum group metal catalysts will, undoubtedly, lead to continuing study and further discussions at the Tenth International Congress on Catalysis to be held in Hungary in 1992.

N.J.G., R.R.R.

Geology and Geochemistry of the Platinum Metals

Platinum-Group Element Exploration, Developments in Economic Geology

BY D. L. BUCHANAN, Elsevier, Amsterdam, 1988, 185 pages, U.S.\$79/Dfl. 150

The price of platinum over the past decade, supported by increasing demand for the metal for industrial, investment and decorative purposes, has helped to stimulate worldwide interest in exploration for the platinum group elements; the publication of this book is therefore timely. It presents a set of guidelines for implementing an exploration programme and assessing the economic potential of an ore

body, and is supplemented by a bibliography of some 130 items. As well as providing mining geologists with a wealth of practical information, much of which is based upon the author's experience of the rocks of the Bushveld Igneous Complex, the book contains information that will be of interest to users of the platinum metals who wish to know of the geological factors that govern their availability.