

First European Congress on Catalysis

By Professor G. C. Bond

Brunel University, Uxbridge, Middlesex

The first European Congress on Catalysis (EUROPACAT I), which was held at the CORUM Conference Centre in Montpellier, France, from the 12th to the 17th September, 1993 coincided with the formation of the European Federation of Catalysis Societies (EFCATS). The Congress and the setting up of the Federation marked the culmination of three years' intensive planning by representatives of almost every European country where catalysis is practised and studied, including those of Eastern Europe and the Commonwealth of Independent States.

EUROPACAT I took the form of fifteen independent symposia covering all branches catalysis, with five running in parallel at any one time; each symposium was organised by one of the national catalysis societies, and a total of about 145 papers were presented. There were also extensive poster displays, the titles of no less than 735 being listed. The meeting was attended by more than 1000 participants, including many from Eastern Europe. The local organisation under the chairmanship of Professor François Figueras coped magnificently with this unexpectedly large attendance.

At least nine of the fifteen symposia featured catalysis by the platinum metals to some extent, and reference is made to some of these contributions below; but the overwhelming importance of this group of metals is well illustrated by the fact that in the symposium on "Catalysis by Metals and Bimetallics" no less than thirteen out of fifteen papers dealt specifically with them. Our attention in this review will therefore naturally be focused on the contents of this particular symposium. Within this group it was also evident that there is a continuing interest in bimetallic systems, which formed the subject of six of the papers.

Monometallic Catalysts

Methods of catalyst preparation continue to receive attention: detailed studies were reported on the interaction of $\text{Pt}(\text{acac})_2$ (1) and of $\text{Rh}(\pi\text{-allyl})_3$ (2) with common oxidic supports such as alumina, silica and titania, various intermedi-

ates in the conversion of these complexes to metallic particles being detected spectroscopically. Koningsberger and colleagues (3) reported a most interesting study of the effect of reduction conditions on the structure and properties of supported metal particles. By the use of EXAFS (Extended X-ray Absorption Fine Structure) they found that at low reduction temperatures there was a layer of chemisorbed hydrogen between the metal (platinum) and the support, and this was irreversibly removed on reduction at 450°C. The capacity of the surface platinum atoms to chemisorb hydrogen was then lowered, because, according to the authors, there was a permanent change in the structure of the metal-support interface, which in turn changed the electronic properties of the metal particles.

Other questions concerning metal-support interactions, and the use of novel and unusual supports, continue to generate interest. Until recently the use of basic supports was not much favoured; it is however known that platinum supported upon magnesia converts alkanes to aromatics with good selectivity, but it is now reported that palladium supported upon magnesia catalysts perform even better (4). This system was also investigated by a "model" technique, that is, condensing palladium vapour onto a magnesium (100) surface (5); the palladium particles had the unique shape of a truncated square pyramid. A first attempt has been made to use buckminsterfullerene as a support for a metal (6); it was first deposited onto a support of higher

area, and then Ru(acac)₃ was used as a source of metal. The resulting catalyst was used for hydrogenation of cinnamaldehyde, giving selectivities to cinnamyl alcohol of about 80 per cent.

The so-called "strong metal-support interaction" still fascinates catalytic chemists. The modification of titania by incorporating higher-valent cations, such as W⁶⁺, produces a support for a rhodium catalyst which is twenty times more active for carbon monoxide hydrogenation than is the unmodified support (7). A method for preparing mesoporous platinum supported upon titania aerogels from Ti(OⁿBu)₄ + PtCl₄ or Pt(acac)₂ was reported (8); the product contained anatase particles about 8 nm in size, and had an area of 200 m²/g. Further evidence for the encapsulation model was obtained by ion-scattering spectroscopy of rhodium supported on titania model catalysts (9).

Catalyst Characterisation

In addition to the methods alluded to above, a number of comparatively novel methods were described for characterising the structure of metallic catalysts. EXAFS is finding ever wider application, but the theoretical interpretation of the observed oscillations is still not firmly established, and failure to allow for the anharmonicity of the motion of atoms in the surface may lead, especially with lighter elements, to an underestimation of the particle size (10). ¹H NMR of hydrogen adsorbed on supported metal catalysts is another rich source of information; when applied to palladium catalysts in conjunction with measurements of uptake, it is capable of distinguishing between the strongly-chemisorbed + α -hydride phase and β -hydride phase (11). Metal surfaces are known to be labile and to reconstruct to minimise surface free energy; but what is surprising is that the background pressure in the residual vacuum under UHV conditions is sufficient to effect an adsorbate-induced reconstruction observable by Scanning Tunnelling Microscopy (12).

Bimetallic Catalysts

The preparation of small, homogeneous alloy particles on supports suitable for catalytic applications still poses a number of difficulties. One

approach is to use as precursor a compound in which the desired elements are linked; for example, the compound (*p*-tolyl)₄Cu₂Rh₂ was used to prepare supported CuRh particles which showed useful properties in liquid-phase reactions (13). Similarly the binuclear acetate-bridged complex PdCu(OAc)₄ has been employed to make Pd-Cu/Al₂O₃ catalysts (14). Pt-Au/SiO₂ catalysts can be made by reacting a reduced platinum on silica catalyst with HAuCl₄, a process that can lead either to the random deposition of gold atoms on the platinum particles, or to a specific coverage of low-index planes, depending on the conditions used (15). Conventional impregnation of silica with solutions of the chlorides of palladium and gold produces materials, the homogeneity of which is uncertain, but careful X-ray Photoelectron Spectroscopy work reveals the presence of Si⁰ close to the small alloy particles after reduction at only 380°C (16).

The ability of the platinum group metals to form sols of finely divided metal particles has been known for many years, but only recently have bimetallic sols been studied. Bimetallic palladium-copper sols, which are supported on carbon are effective catalysts for hydrogenating alkynic alcohols (17).

Applications as Catalysts

Mention of metal sols as supported metal catalyst precursors leads us naturally to their use in unsupported form; rhodium particles prepared under phase-transfer conditions show high stereoselectivity for reducing *ortho*-disubstituted aromatic rings to *cis*-disubstituted cyclohexanes (18). Crown ethers containing benzene rings fused into the macrocycle can be similarly reduced. A most interesting innovation is the use of an osmium tetroxide complex with an alkaloid, such as cinchonidine, incorporated in a polymeric matrix, as a catalyst for enantioselective di-hydroxylation of alkenes (19). Chiral palladium complexes containing neutral bidentate optically-active nitrogen ligands effect enantioselective allylic substitutions.

One symposium was devoted to "Catalysis and the Environment", and not surprisingly the

selective reduction of nitrogen oxides featured in a number of papers. Although vanadia-titania catalysts and copper-exchanged ZSM-5 zeolite are effective, attention is now turning to lean-burn conditions, where catalysts based on the platinum group metals have potential (20). There were also several studies reported of the kinetics and mechanism of the nitric oxide-carbon monoxide reaction. On rhodium single crystal surfaces, nitric oxide is strongly chemisorbed and blocks access of carbon monoxide to the surface: their reaction is therefore slower than is the oxidation of carbon monoxide (21). Bimetallic combinations involving palladium were compared with rhodium; the palladium-chromium showed comparable activity, but palladium-silver was less active (22).

Fundamental investigations enlarging our understanding of catalysis were comparatively few in number. The use of transient kinetic methods to study the methane-deuterium equilibration on Rh-Ag/SiO₂ catalysts revealed that the desorption rate of C₁ species was faster than over rhodium supported on silica, and the strength of hydrogen chemisorption less (23). The reasons underlying the dependence of activity on the size of metallic particles have long been questioned by catalytic scientists. It

now appears possible that the effect may have an energetic rather than a geometric explanation, for a particle-size dependence of reaction kinetics in alkane hydrogenolysis has been traced to differences in hydrogen chemisorption strength (24).

The concept of using a semi-permeable membrane to overcome equilibrium limitations, for example, in dehydrogenations, is also not new, but no practical application on any scale has yet resulted: attempts to develop usable systems are however continuing. Palladium-silver membranes used for isobutane dehydrogenation are unfortunately quickly poisoned (25), but efforts to construct membranes from platinum supported on alumina are showing promise (26, 27).

Conclusion

It has only been possible to mention a few of the highlights of the papers presented at EUROPACAT-I, and scarcely any of the many posters which featured the platinum group metals. However, it is clear that they continue to dominate the catalytic scene, and that their efficiency in very many applications remains unchallenged. EUROPACAT-II will be held in Maastricht in September 1995: put that date in your diary now.

Speakers

- 1 S. Köhler, S. Trautmann, H. Doopsch and M. Baerns, Universität Bochum, Germany
- 2 P. Dufour, C. C. Santini, S. L. Scott and J. M. Basset, I. R. C. and Ecole Supérieure de Chimie Industrielle de Lyon, France
- 3 D. C. Koningsberger, M. Vaarkamp, F. S. Modica and J. T. Miller, Utrecht and Eindhoven Universities, The Netherlands, and Amoco Research Center, Naperville, IL, U.S.A.
- 4 E. G. Derouane, V. Jullien-Lardot, A. Pasau-Claerbout, N. J. Blom and P. E. Højlund Nielsen, Facultés Universitaires, Namur, and Haldor Topsøe Research Laboratories, Lyngby, Denmark
- 5 C. R. Henry, C. Chapon, C. Duriez and R. Monot, CNRS Campus de Luminy, Marseille, France, and EPFL, Lausanne, Switzerland
- 6 J. M. Planeix, N. Coustel, B. Coq, P. Kumbahr, R. Dutartre and P. Geneste, ENSCM, Montpellier, France
- 7 T. Ioannides, Z. Zhang, A. M. Efstathiou and X. T. Verykios, University of Patras, Greece
- 8 M. Schneider, T. Mallát, D. G. Duff and A. Baiker, ETH, Zürich, Switzerland
- 9 C. Linsmeier, H. Knözinger and E. Taglauer, Max-Planck-Institut für Plasmaphysik, Garching, Germany, and Universität München, Germany
- 10 B. S. Clausen, H. Topsøe, L. B. Hansen, P. Stolze and J. K. Nørskov, Haldor Topsøe and Technical University of Denmark, Lyngby, Denmark
- 11 M. Polisset, D. Roubah, P. J. Levy, M. A. Springuel-Huet and J. Fraissard, Université Louis Pasteur, Strasbourg, France
- 12 P. Legare, G. Maire, P. Bernhardt and F. Pflanz, Université Louis Pasteur, Strasbourg, France
- 13 K. van Gorp, D. M. Grove, J. T. B. H. Jastrzebski, G. van Koten and J. W. Geus, University of Utrecht, The Netherlands
- 14 L. V. Nosova, V. I. Zaikovskii, A. V. Kalinkin and Yu. A. Ryndin, Institute of Catalysis, Novosibirsk, Russia
- 15 J. Barbier, P. Marecot, G. del Angel, P. Bosch and M. Dominguez, Université de Poitiers, France, and Universidad Autonoma Metropolitana Iztapalapa and Instituto Mexicano de Petroleo, Mexico

- 16 W. Juszczyk, Z. Karpiński, D. Lomot, J. Pielaszek and J. W. Sobczak, Institute of Physical Chemistry, Warsaw, Poland
- 17 N. A. Zakarina and M. K. Saimerdenova, Institute of Organic Chemistry and Electrochemistry, Alma Ata, Kazakhstan
- 18 K. Nasar, P. Drogat-Landre, F. Fache, M. Besson, D. Richard, P. Gallezot and M. Lemaire, VCBL and IRC, Villeurbanne, France
- 19 D. Pini, A. Petri and P. Salvadori, Università di Pisa, Italy
- 20 R. Burch, P. J. Millington and A. P. Walker, University of Reading and Johnson Matthey Technology Centre, U.K.
- 21 Q. Gao, Y. Li, M. Bowker and R. W. Joyner, University of Liverpool, U.K.
- 22 A. el Hamdaoui, J. Massardier, M. Primet and A. Renouprez, IRC, Villeurbanne, France
- 23 L. Seyfried, J. M. Bastin, M. Nouinou and A. Frennet, Université Libre de Bruxelles, Belgium
- 24 G. C. Bond and J. C. Slaat, Brunel University, Uxbridge, U.K.
- 25 P. E. Højlund Nielsen, S. Laegsard Jørgensen and P. Lehrmann, Haldor Topsøe, Lyngby, Denmark
- 26 J. Peureux, M. Torres, A. Giror-Fendler, H. Mozzanega, J. Sanchez and J. A. Dalmon, IRC and Lab. d'Automatique et de Genie de Procédés, Villeurbanne, France
- 27 G. Capanelli, A. Bottino, A. Grosso, A. Servida, G. Vitulli, A. Mastantuono, R. Lazzoroni and P. Salvadori, Universities of Genova and Pisa, Italy

Methane Conversion Using Platinum Loaded Zeolites

The ability to convert methane to higher alkanes directly would be of value industrially for the production of liquid fuels and chemicals. Recently a two-step process has been reported for higher alkane production from methane using a platinum, ruthenium or cobalt catalyst supported on silica. In the first step the metal is exposed to flowing methane and in the second step the alkanes are released from the surface by flowing hydrogen. Related work on alkane production has also been reported when the second step was performed at a lower temperature than the first step. However, this is a stoichiometric reaction, and is not truly catalytic, and only one monolayer of C_1 is converted at each cycle. The methane also sweeps away hydrogen from the surface, allowing hydrogen deficient species to build up and carbon-carbon bonds to form. For this reaction large surface areas are needed, which will allow reasonable levels of methane conversion to occur.

One way to achieve large surface areas is by using zeolites and filling the cages with the reaction metals. Zeolites are extensively used as catalyst supports, particularly faujasites, as they produce very homogeneously dispersed catalysts with down to nearly atomic sized particles.

Therefore, preliminary work has been undertaken on methane conversion. (E. Mielczarski, S. Monteverdi, A. Amariglio and H. Amariglio, *Appl. Catal. A: Gen.*, 1993, **104**, (2), 215–228). Experiments were carried out by a methane adsorption and a hydrogenation step. Alkanes produced included ethane, propane, *n*- and *i*-butane, *n*-, cyclo- and *i*-pentane and *n*-, cyclo- and other isomers of hexanes and traces of heptanes. Hydrogenolysis was also monitored. At higher reaction temperatures, with Pt/HX, the total amount of homologated methane increased significantly with temperature, even though

hydrogenolysis increased, at the expense of higher alkanes. On Pt/HY the amount of homologated methane reached a maximum at about 275°C but the yield decreased from 52 to 30 per cent when the temperature increased from 250 to 325°C. Hydrogenolysis occurred mainly in the range 250–350°C and was less for Pt/HX than for Pt/HY. The results were compared to those for EUROPT-1 for the same 6 per cent platinum loading. The molar amount of methane homologated in identical operating conditions shows that the catalyst efficiencies are in the order Pt/HX > Pt/HY > EUROPT-1

It is concluded that the beneficial effects of using zeolites for direct methane conversion could be increased by using NaX or NaY zeolites, which should have less hydrogenolysis activity, by performing the reaction sequence at higher temperatures, and by adding a second metallic component to the platinum.

Ruthenium-Niobium-Zirconium System

Efforts to improve the physical properties of alloys have generally proceeded in a quasi-empirical way, but there is a need to improve on the trial and error approach particularly now that materials with special combinations of mechanical and electronic properties are required. As part of a programme to advance the design of intermetallics, a study has been made by researchers at The University of Texas at Austin of the phase stability for the three binary systems of the ruthenium-niobium-zirconium ternary system using first-principles methods (J. D. Becker and J. M. Sanchez, *Mater. Sci. Eng.*, 1993, **A170**, (1–2), 161–167).

The accuracy in calculating properties such as Debye temperature, formation energy and solubility, without empirical input, highlights the potential of this approach to alloy development.