

5th European Congress on Catalysis

EUROPACAT-V DEMONSTRATES THE TREMENDOUS INTEREST IN CATALYSIS

The 5th European Congress on Catalysis (EuropaCat-V) took place in Limerick, Ireland, from the 2nd to 7th September, 2001. The attendance of over 1000 delegates from 52 countries heard and viewed some 1170 oral and poster presentations. Five plenary lectures highlighted key areas of research and development in catalysis, and other oral presentations were grouped into 7 parallel sessions of 21 different symposia. These covered most areas of heterogeneous catalysis from fundamental catalysis and surface science to industrial catalysis. There was also a strong contribution from the homogeneous catalysis community – including bio-catalysis. This selective review looks at the platinum metals work reported at the conference.

Fundamental Catalysis and Surface Science

Professor David King (University of Cambridge, U.K.) opened the conference with a review of the contribution made by his group to a fundamental understanding of three key reactions: ammonia oxidation over platinum, ethane epoxidation over silver and methane partial oxidation on platinum. The reactions were analysed using a range of surface science techniques with single crystal metal substrates. As well as more established techniques, Professor King also discussed data from his ground-breaking microcalorimetry experiments which allow the measurement of heats of adsorption for fractions of a monolayer of adsorbate.

Further talks in this symposium discussed the latest advances in surface science studies of model catalyst systems. Professor Hans-Joachim Freund (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin) described his work on preparing thin alumina films through the oxidation of a Ni/Al alloy single crystal. The alumina film (~ 4 monolayers thick) is then sufficiently conducting to allow use of conventional electron-based surface science tools. Model catalyst systems can also be prepared

by metal deposition onto the oxide, and an example using rhodium was given.

Claude R. Henry (CRMC2-CNRS, Marseille) used a different approach starting with a bulk MgO single crystal onto which palladium was deposited. As the substrate is non-conducting the range of analytical tools which can be applied is limited but atomic force microscopy can yield information on particle morphology.

Environmental Catalysis

In a keynote lecture, A. P. Walker (Johnson Matthey, U.K.) gave a broad ranging overview of autocatalysts past and present and outlined the future requirements for lean burn catalyst systems, particularly for the control of nitrogen oxides (NO_x) and particulate. He extended a challenge to the academic community by stressing that catalyst improvements were still required and welcomed any new ideas.

A large number of papers were devoted to NO_x reduction using hydrocarbon in excess oxygen. Unfortunately the wide range of experimental conditions often makes it difficult to compare the activity of novel catalyst systems with more established ones. According to M. Maciejewski (ETH, Zürich) iridium black exhibited good NO_x conversion with propene at 400–450°C, with larger crystallite size giving a better selectivity to nitrogen. Dimitris I. Kondarides (University of Patras, Greece) presented a mechanistic study of the NO/C₃H₆ reaction in the presence of oxygen over Rh/TiO₂ using FTIR spectroscopy. Under reaction conditions he suggested that partial rhodium oxidation inhibited NO_x reduction compared with the oxygen-free system.

In the symposium on catalysis for green chemistry, Steve Bennett (Johnson Matthey, U.K.) gave a talk entitled 'Selective oxidation of alcohols with anchored homogeneous catalysts'. He introduced the use of FibreCat™ supported ruthenates and perruthenates as anchored homogeneous catalysts for selective oxidation reactions, and compared

them to a range of carbon-supported platinum group metal heterogeneous catalysts also from Johnson Matthey. He showed preliminary results of the use of OsO₄ supported on FibreCat™ on the dihydroxylation of alkenes. This technology allows the easy handling of OsO₄ (toxic and highly volatile in its free state, but stabilised by anchoring to FibreCat™) for use in dihydroxylation reactions.

Combinatorial Catalysis and High Throughput Screening

The symposium on combinatorial catalysis and high throughput screening was preceded by a plenary lecture from Henry Weinberg (Symyx Technologies, U.S.A.) describing the facilities at Symyx for combinatorial catalyst production, and high throughput screening and characterisation in both homogeneous and heterogeneous catalysis. He described the principles of the methodology adopted with primary screening in which a simplified preparative and test procedure was used to give a 'yes/no' distinction between catalysts. This primary screening could be carried out on up to 1000 catalysts per day. Candidates selected for secondary screening were tested with more realistic conditions – up to 100 per day.

Professor Ferdi Schuth (Max-Planck-Institut für Kohlenforschung, Germany) described their excellent facilities, stressing the need to combine reproducible synthesis and good reactor engineering with the informatics for large data sets. As a working example he described screening for lean NO_x catalysts. Large numbers of oxide supports were produced by impregnating activated carbon followed by calcination, and quantitative reactivity measurements were made using a NO_x-sensitive dye. Alternatively, a spatially resolving IR detector could be used on the outlet of a 16-cell parallel-screening reactor.

Industrial Catalysis

Colin Gent (iAc, U.K.) delivered the keynote lecture 'Industrial catalysis – a view from industry'. He predicted extensive amalgamation of existing chemical companies, resulting in a far smaller number. He saw universities producing fundamen-

tal research – which would cease to be carried out by industry – but saw the need for stronger links and closer cooperation between the two. He foresaw that future important trends would include the need to reduce waste/pollution and improve energy efficiency – the price of failing to do so is gradually becoming more significant.

The plenary lecture prior to the industrial catalysis symposium was given by John N. Armor (Air Products & Chemicals, U.S.A.) speaking on 'Opportunities, strategies and innovation for catalysis in the new millennium'. He identified a number of areas which he expected to be of crucial importance in coming years. These included: photocatalytic water splitting to generate hydrogen for fuel cell vehicles, more use of combinatorial catalysis with high throughput screening supported by the informatics to generate an extensive catalysis data bank, asymmetric synthesis, nanotechnology, and catalysis for fine chemicals. Armor also suggested that improved cooperation between catalytic chemists and molecular biologists could be an important step in improving the exploitation of enzymatic catalysis and in producing synthetic enzymes (biomimetics).

Biomimetics was also covered in a plenary lecture by Professor A. E. Shilov (Institute of Biochemical Physics, Moscow) who showed how the general principles of enzymatic catalysis together with an understanding of the mechanism of certain enzymes can be used to find new catalysts and develop improved catalytic performance.

Fuel Processing

Oral presentations on fuel cells for automotive applications featured in several of the symposia. The symposium on hydrocarbon valorisation was introduced by a keynote lecture presented by Josefin Meusinger (Global Alternative Propulsion Center GM and Adam Opel AG, Germany), who spoke on fuel cell vehicles at General Motors/Opel. She explained that although the hydrogen fuel cell vehicle has been demonstrated and is currently under development, without a hydrogen economy several obstacles remain to storing hydrogen onboard a vehicle. Onboard hydrogen storage as either liquid or compressed

gas is not considered feasible. However, onboard reforming of hydrocarbons to generate hydrogen is being implemented as a short-term solution. General Motors/Opel is concentrating its resources on gasoline reforming since the necessary distribution infrastructure is already in place. Modifying the existing infrastructure to distribute methanol as a fuel for reformer vehicles is not thought to be viable. For this reason General Motors has ceased to work on methanol reforming despite its comparative ease.

Shell's technology on catalytic partial oxidation (CPO) of hydrocarbons was described in a keynote lecture by Professor G. J. Kramer (Shell, The Netherlands) during the symposium on alkane activation. Shell Hydrogen, in collaboration with International Fuel Cells, is working on fuel processing technology. Kramer outlined the characteristics of the CPO technology with methane, indicating that the process is carried out in a mass-transfer limited mode of operation. CPO technology would then be developed further so

that other feedstock would be included.

To sum up, this was an extremely interesting congress with broad coverage and the participation of leading industry and academic figures describing their technology and contributing ideas. At the time of writing the conference abstracts are still available at the European Federation of Catalysis Societies (EFCATS) website (www.efcats.org).

The venue of the 6th EuropaCat conference will be in Garmisch-Partenkirchen in the South German Alps, organised under the auspices of EFCATS. The conference is scheduled to take place from 14th to 18th September, 2003, and will be a joint event run by the Catalysis Societies of Austria, Germany and Switzerland, see website www.europacat.org.

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Aerobic Oxidation of Alcohols with Palladium-Hydrotalcite

The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively, plays an important part in organic synthesis. Traditionally, such transformations have been performed with stoichiometric quantities of oxidants, such as chromium salts, oxalyl chloride, and so on. These work well in small-scale reactions, however on an industrial scale, there is a waste of heavy metals and unwanted coproducts, so the search for effective cleaner catalytic systems which use inexpensive primary oxidants such as molecular oxygen, hydrogen peroxide and/or air (a 'green method') for oxidising alcohols to aldehydes and ketones, remains an important challenge. Several metal catalysts, including Pt, Pd, Ru, Co, Cu, V, Os, Ce and Ni, have all been reported for this system, with Pd being used to advantage with pressurised air. A system using homogeneous palladium acetate has also been reported for the aerobic oxidation of alcohols using pure oxygen.

The scientists who developed the latter system, working at the Department of Energy and

Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Japan, have now prepared and successfully used a palladium(II) acetate-pyridine hydrotalcite catalyst to oxidise alcohols to aldehydes and ketones using air as sole oxidant at 65°C (N. Kakiuchi, Y. Maeda, T. Nishimura and S. Uemura, *J. Org. Chem.*, 2001, 66, (20), 6620–6625).

Palladium(II) acetate-pyridine was readily supported on hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$, a clay mineral, to give a heterogeneous palladium catalyst. With this catalyst alcohols could be oxidised at a lower temperature using air at atmospheric pressure instead of pure oxygen. A variety of primary and secondary alcohols, such as benzyl alcohol and dodecan-1-ol, in toluene were oxidised to the corresponding aldehydes and ketones in high yield. Allylic alcohols, such as geraniol and nerol, were effectively oxidised without any alkenic isomerisation. The catalyst can be easily recovered and reused several times and leaching of the Pd(II) species could be avoided.