

7th European Congress on Catalysis

ACADEMIC AND INDUSTRIAL ADVANCES ON ALL FRONTS IN PGM HETEROGENEOUS CATALYSIS

By Stephen Poulston*, Andrew Smith** and Thomas Ilkenhans***

Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, U.K.;

*E-mail: poulss@matthey.com; **E-mail: smithawj@matthey.com; ***E-mail: ilkent@matthey.com

The 7th European Congress on Catalysis (EUROPACAT-VII – A Key to a Richer and Cleaner Society), organised by the Bulgarian Catalysis Club and the Greek Catalysis Society under the auspices of the European Federation of Catalysis Societies (EFCATS) took place in Sophia, Bulgaria, from the 28th August to 1st September, 2005. In all there were 773 registered delegates from 39 countries and 750 presentations – 170 oral and 580 posters. At the end of each oral session, selected posters were described in two-minute flash oral presentations, and 200 posters were covered in this way. The oral presentations were grouped into 11 different symposia covering most areas of heterogeneous catalysis from fundamental catalysis and surface science to industrial catalysis.

Several symposia featured work on the platinum group metals, and the papers reported here are grouped into very general categories.

EFCATS Sponsored Awards

Two awards are made at this Congress. One is the Johnson Matthey Award for Innovation in Catalysis, which was awarded to Professor Valentin N. Parmon of the Boreskov Institute of Catalysis, Novosibirsk, Russia. The other award is the François Gault Lectureship, and Professor Graham Hutchings of Cardiff University, U.K. became the award holder for 2006. The holder of this position acts as an ambassador for catalysis by lecturing around Europe.

Catalyst Preparation

A one-step flame synthesis route to Pt/Ba/Al₂O₃ was described by Reto Strobel (ETH Zurich, Switzerland). The material was prepared using two flame spray pyrolysis nozzles, one for the Al precursor and the other for the Pt/Ba precursors. The resulting material was found to have

good NO_x storage capacity. However, material made with only one nozzle for the Pt, Ba and Al had no NO_x storage capacity.

Plasma spraying and cold gas dynamic spray methods used in preparing palladium (Pd), Pd-Mn, Cu-Cr and Mn catalysts for methane combustion were described by O. Yu. Podyacheva and coworkers (Boreskov Institute of Catalysis), and O. P. Solonenko and V. F. Kosarev (Institute of Theoretical and Applied Mechanics, Novosibirsk, Russia). The cold gas method was employed to deposit the metals onto thin metal foils, although other types of support, such as sheet, metal plate and foam were also discussed. In the procedure, a layer of alumina was deposited onto the metal surface for good adhesion, this was followed by a second alumina phase, and then the catalyst. Samples were characterised by XRD, SEM and XPS. SEM and thermal testing confirmed excellent adhesion and thermal stability. It was suggested that the samples could be suitable for use in the catalytic chambers of gas turbines.

The design of a Pd/carbon coated asymmetric α-Al₂O₃ membrane catalyst for the production of hydrogen peroxide (H₂O₂) by direct synthesis was described by S. Melada and colleagues (University of Venezia, Italy) and G. Centi (University of Messina, Italy). The procedure involved coating an alumina tube with a ceramic layer then a carbon layer, followed by Pd deposition. The effect of the Pd oxidation state, H₂ partial pressure and synthesis variables were discussed. Results indicated that both a high partial pressure of hydrogen and surface oxidised Pd particles were needed for high activity. H₂O₂ is extensively used in the pulp paper/textile industries and is currently produced by the anthraquinone process. This process is not ideal, but other methods of production need to

*direct synthesis
of hydrogen
peroxide*

The Johnson Matthey Award for Innovation in Catalysis



Professor Valentin N. Parmon holding the award. On his left is the Chairman of EFCATS, Professor Gabriele Centi (University of Messina, Italy), and on his right is John L. Casci (Johnson Matthey Catalysts) who presented the award

The Johnson Matthey sponsored “Innovation in Catalysis” award has been presented now at three EURO PACAT meetings. At EURO PACAT-VII, Professor Valentin Parmon of the Boreskov Institute of Catalysis, Novosibirsk, Russia, was granted the award for “his fundamental contribution to the development of catalytic and photocatalytic solutions to sustainable processes and energy”. The award is managed and administered by the European Federation of Catalyst Societies.

At EURO PACAT-V the award was conferred on Pierre Jacobs (Katholieke Universiteit Leuven, Belgium) and at EURO PACAT-VI on Giuseppe Bellussi (EniTecnologie, Italy).

consider that potentially explosive mixtures can be generated on scale-up. As the demand for H_2O_2 is likely to increase in the future (2M tonnes production in 2003), alternative production routes are certainly of commercial interest.

Catalyst Characterisation

Professor M. Neurock (University of Virginia, U.S.A.) gave a plenary lecture entitled ‘First-principles elucidation and design of catalytic sites and their environments’. He discussed the necessity for understanding, on an atomic scale, the active sites that control catalytic behaviour and their local reaction environment, as both are important in the search for more active and selective catalysts. Defect surface sites, bimetallic alloys, promoters, poisons, coadsorbed intermediates and the catalyst support can all change the nature of the adsorbate/surface interactions. Professor Neurock used *ab initio* quantum mechanical methods and theory to study alloys for catalytic and electrocatalytic systems, including lean NO_x catalysis.

Professor R. Schlogl (Fritz Haber Institute, Berlin, Germany) emphasised the need for both static and dynamic characterisation of catalysts to

improve functional understanding of catalytic systems. One example used to illustrate this was the selective hydrogenation of pentynes over a range of Pd surfaces: single crystal Pd(111), Pd foil and Pd/alumina. High resolution XPS identified the presence of surface, sub-surface and bulk dissolved carbon.

Microscopy with ‘SuperSTEM’ (scanning transmission electron microscope) was described by J. L. Casci (Johnson Matthey Catalysts, Billingham, U.K.) for characterising promoters in cobalt Fisher-Tropsch catalysts. The technique is capable of sub-Ångstrom resolution, and was used to find the location of promoter atoms in the Co/alumina catalyst. Catalyst samples, prepared by the cobalt ammine carbonate deposition-precipitation method, were post-impregnated with Pt, Ir, Re or Ru precursors. A high-angle annular dark-field detector produced atomic number contrast imaging, while electron energy-loss spectroscopy (EELS) was used for elemental spectroscopy. The Pt, Ir and Re promoters were mainly present as isolated atoms, while the Ru promoter was present both as isolated atoms and in regions of high concentration with Co particles. All four elements

promoted the reduction to metallic cobalt, but only Ru, Pt and Ir were effective in lowering the temperature of the Co_3O_4 to CoO transition. Later analysis, including *in situ* XRD, showed the reduction of Co_3O_4 to CoO to Co metal.

R. N. Devi (Queen's University of Belfast, U.K.) presented work on preparative aspects of a 5% Pt-0.5% Fe catalyst coated with Na-A zeolite for the selective oxidation of CO in the presence of *n*-butane. The zeolite coating allows the CO to reach the Pt catalyst but inhibits the *n*-butane. This leads to a big difference in the catalyst light-off temperature.

Theoretical Methods and Fundamental Studies

Professor R. Burch (Queen's University Belfast, U.K.) stressed, as did many presenters, the need for *in situ* characterisation to identify reaction mechanisms. Steady state isotopic transient kinetic (SSITK) measurements were combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to look at the forward and reverse water gas shift reaction over Pt/ CeO_2 . The DRIFTS equipment was designed to minimise residence time, in order to give a time resolution of a few seconds, and to prevent gas bypassing the catalyst to give improved kinetic data. The data showed that the carbonyl and carbonate species on the catalyst surface decayed at the same rate as the labelled CO, but that formate decayed much more slowly, indicating it was a minor intermediate in the reaction pathway under the conditions used.

C. R. Henry (CRMCN-CNRS, Marseille, France) described a surface science approach for producing a model supported catalyst. A Ni_3Al (111) single crystal was oxidised at 1000 K to give an alumina film surface with a regular array of defects. Pd was deposited, and then gold (Au), and the bimetallic particles gave an ordered array of clusters. The spatial distribution of the Au and Pd is controlled by the surface defects.

Photocatalysis

Two talks examined light-sensitive precious metals-promoted titania systems for hydrogen production. The first talk, by M. Kitano (Kansai

University, Japan), described a visible light-responsive Pt/ TiO_2 thin film photocatalyst produced by magnetron sputtering of Pt onto a planar TiO_2 substrate. This configuration allowed the Pt and TiO_2 sides of the catalyst to be physically separate, to prevent recombination of the O_2 (produced on the TiO_2) and the H_2 (produced on the Pt), and thus easy separation of the two gases. The titania was a mixture of rutile and anatase, and the coating procedure produced TiO_2 slightly reduced at the surface. The TiO_2 was sensitive to visible light.

The second talk, by Professor M. J. Bowker (University of Cardiff, U.K.) described a Pd/ TiO_2 (P25) photocatalyst for reforming methanol to H_2 and CO_2 using UV light. The Pd loading had a strong influence on activity, which reached a maximum at 0.5 wt.% Pd.

The photocatalysed degradation of pesticides and organic pollutants was discussed by D. Bahnemann (University of Hanover, Germany), and M. Muneer and colleagues (Aligarh Muslim University, India). They examined the degradation of pesticide derivatives, such as *N,N*-dimethyl- α -phenyl benzene acetamide (diphenamid), bromacil, terbacil and 2,4,5-tribromoimidazole (TBI), and other pollutants, such as benzidine. Aqueous suspensions of TiO_2 were investigated under varying conditions of pH, substrate, photocatalyst concentration, type of TiO_2 and the presence of H_2O_2 as an alternative additive to O_2 . Several factors were found to be important for electron transfer and it was speculated that in order to improve the electronic effects in the reaction, mixed semiconductors ($\text{TiO}_2/\text{SnO}_2$) and Pt, Pd, Au or Ag might have to be included.

*photocatalysed
pesticide
and organic
pollutant
degradation*

Catalyst Deactivation as Part of Catalyst Design

Professor S. D. Jackson (University of Glasgow, U.K.) highlighted the role of catalyst deactivation as a key part of catalyst design. Examples of catalyst deactivation in industrial processes were given, including propane dehydrogenation for which Pt and Cr catalysts were compared. Both catalysts deactivate quite rapidly,

Pt in 3 to 5 days, and Cr in 15 to 25 minutes. Processes have been designed to manage this deactivation, for instance, the Oleflex process (propane to propylene) from UOP using a Pt catalyst, and the Catofin[®] process from Houdry, using a Cr-based catalyst.

Fine Chemical Synthesis

Two presentations examined the use of precious metal catalysts for the synthesis of fine chemicals and their intermediates.

H. Markus and colleagues (Åbo Akademi University, Turku, Finland) discussed the use of Pd supported on zeolites for the hydrogenolysis of the lignan hydroxymatairesinol to matairesinol (matairesinol is an anticarcinogenic and antioxidative lignan). The work described the extraction of hydroxylmatairesinol from Norway spruce (*Picea abies*) knots, which in 1998 were found to contain up to 10% lignans, with hydroxymatairesinol being the most abundant. The synthesis was carried out in a stirred glass reactor under hydrogen flow with 2-propanol as the solvent. Several Pd/zeolite catalysts were investigated and characterised by metal dispersion, surface area, support acidity, pore size and metal content. A bifunctional mechanism for the hydrogenolysis was proposed, requiring both metal and acid sites. Relatively large pores in the zeolite were considered important to allow the bulky reactant molecules access to the active sites. The results indicated that the reaction rate was inversely dependent on the acidity of the supporting zeolite.

*matairesinol
production*

E. Sulman and coworkers (Tver Technical University, Russia), P. Valetsky and colleagues (Nesmayanov Institute of Organoelement Compounds, Moscow, Russia), and P. Valetsky and L. Bronstein (Indiana University, U.S.A.) discussed the synthesis of vitamin intermediates and fragrant substances by metal-polymeric nanocatalysts. They looked at the use of stabilised precious metal nanoparticles for achieving high selectivity, activity and technological performance. Different types of metal-polymeric catalysts, in Pd, PdZn and PdPt systems, were reviewed and the impor-

*synthesis of
vitamin
intermediates*

tance of the stabiliser towards activity was emphasised. They claimed improved activity and good selectivity, compared to a commercially available Pd catalyst.

Environmental Catalysis

Professor R. Prins (ETH Zurich, Switzerland) gave a plenary lecture on 'Hydrotreating catalysis: a contribution to cleaner air'. He discussed hydrodesulfurisation (HDS) and hydrodearomatisation (HDA) over pgm/alumina catalysts. Although systems based on MoS₂ are the main candidates for HDS catalysts, pgm-based catalysts may be useful to further reduce the sulfur levels in a secondary sulfur removal step. At 300°C and 50 atm the order of catalyst activity for the hydrogenation of dibenzothiophene (to produce mostly biphenyl) was found to be: Pd-Pt alloy > Pt > Pd. When the more sterically hindered 4,6-dimethyldibenzothiophene underwent HDS, Pd gave a better performance than Pt, and Pd also produced much stronger hydrogenation, in this case giving predominantly 3,3-dimethylbicyclohexyl.

Work on a reformer for producing hydrogen from dimethyl ether was described by L. J. Pettersson (KTH-Royal Institute of Technology, Stockholm, Sweden). The hydrogen could then be used for catalyst regeneration (such as in a NO_x trap) and to feed PEM fuel cells acting as auxiliary power units. The latter could, for example, provide power to run air conditioning at idle.

The leaching of nitrates from soil into water supplies is known to be due to excessive use of nitrate-based fertilisers in agriculture. In 1998 the European Environmental Agency estimated that 87% of the agricultural land in the EU has nitrate concentrations above the guide level of 25 ppm. The EU has set an upper level of 50 ppm as the maximum permitted concentration of nitrates in drinking water, and amounts above this are deemed unacceptable. One method of nitrate removal is to convert the nitrate ions into nitrogen. This can be achieved by liquid phase nitrate hydrogenation over, generally, heterogeneous bimetallic catalysts. However, more recent work has looked at monometallic catalysts with a

*nitrates
leach into
ground
water*

semiconducting support, such as TiO₂. Professor J. A. Anderson (Aberdeen University, U.K.) presented work aimed at developing procedures to improve understanding of the catalyst under working conditions. He gave results of *in situ* FTIR and XAS examination of Pd/TiO₂ catalyst used to hydrogenate nitrates in aqueous solution. The Pd/TiO₂ catalyst was prepared from TiO₂ P25 (Degussa) and a Pd precursor (Johnson Matthey). His results suggested that the catalyst converts nitrates to N₂ without forming the nitrite. However, the selectivity was considered inadequate.

Work on hydrogenation and oxidation reactions on core-shell nanoparticles of Pd-Ni/MgO was presented by S. Sao Joao and colleagues (CRMCN-CNRS, France), and L. Piccolo and C. R. Henry (IRC-2, France). Generally, the deposition of a thin layer of metal A onto a bulk metal B is known to alter the valence band of bulk B due to coordination, the lattice strain of metal A and the nature of the metals. In this work, a Ni core was prepared on MgO, and Pd was deposited onto the surface by bubbling hydrogen through the precursors (Pd acetylacetonate and Ni/MgO) in toluene. TEM analysis showed the core-shell structure of a Pd shell around the Ni core. The materials were tested for butadiene hydrogenation and CO oxidation.

Electrochemical Promotion

Several presentations focused on the phenomenon of electrochemical promotion (EP), also known as NEMCA (non-Faradaic electrochemical modification of catalytic activity). This relies on the application of a potential across an ionic conductor to alter its surface composition. The conductor carries a deposited catalytic metal, and the altered composition affects the activity of the catalyst. Professor Richard Lambert (Cambridge University, U.K.) illustrated the EP effect with a substrate of ion conducting β "-alumina, where Na or K is pumped to and from the surface on application of potential. Several applications were discussed, including a Fischer-Tropsch reaction over Rh coated K- β "-alumina. The K promotion led to an increase in ethanol production. Recent work was also described on using Pt coated Na- β "-alumina

as a NO_x storage device (analogous to those used in automotive applications for NO_x removal in lean burn engines) where the nitrate can be decomposed by pumping Na away from Pt on application of voltage.

A breakthrough in the practical applications for EP was presented by Professor Costas Vayenas (University of Patras, Greece) who described a monolith-type reactor consisting of 22 parallel plates of YSZ coated on one side with Pt and on the other with Rh. This would allow for the processing of large volumes of gas without significant bypass issues, in a compact device.

Conclusion

The vitality, breadth, and success in research and development in heterogeneous catalysis with the platinum group metals was well demonstrated at this congress.

The next congress, EUROPACAT-VIII, entitled 'From Theory to Industrial Practice' will be held from 26th to 31st August 2007, in Finland at Turku/Åbo. It will be run by the Nordic Catalysis Society, and will be a joint effort by Denmark, Finland, Norway and Sweden. More information can be found from: <http://www.europacat.org/>

The Reviewers



Stephen Poulston is a Principal Scientist at the Johnson Matthey Technology Centre (JMTC), Sonning Common, U.K. He works in the Gas Phase Catalysis Group. His main interests lie in heterogeneous catalysts.



Dr Andrew W. J. Smith is a Senior Scientist in the Gas Phase Catalysis Group at JMTC. He is a synthetic inorganic chemist with experience of materials and catalyst preparation. He is interested in developing new materials and their applications in heterogeneous catalysis.



Thomas Ilkenhans is a Research Chemist in the Gas Phase Catalysis Group at JMTC. He is interested in using palladium in catalysis.