

# EuropaCat IX

The role of platinum group metals in catalysis for a sustainable world

doi:10.1595/147106710X495131

<http://www.platinummetalsreview.com/>

**Reviewed by Juan R. González-Velasco\*, M. Pilar González-Marcos and Beñat Pereda-Ayo**

Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country, PO Box 644, E-48080 Bilbao, Bizkaia, Spain;

\*E-mail: [juanra.gonzalezvelasco@ehu.es](mailto:juanra.gonzalezvelasco@ehu.es)

The biennial European Federation of Catalysis Societies (EFCATS) conference entitled 'Catalysis for a Sustainable World' took place from 30th August to 4th September 2009, in the Convention Center of Castilla and León, in the town of Salamanca, Spain, and was jointly organised by the Spanish Society of Catalysis and the Catalysis Division of the Portuguese Chemical Society. Around 1200 scientists, chemists and chemical engineers discussed the latest results and advances aimed at improving the sustainability of catalytic processes, including the development of more selective catalysts and the minimisation of byproducts; the elimination of pollutants and/or undesired products; the exploration of new energy vectors and the rational use of energy; and the design, characterisation and recovery of catalysts. Attendees from academia and the petroleum, chemical, energy and environmental industries came from fifty countries around the world (85% from European countries and 15% from non-European countries, mainly the USA, Japan and South America). An exhibition showing the products of about twenty companies from catalyst suppliers to instrument manufacturers was located in the same area.

Prominent scientists gave six plenary lectures, twenty-seven keynote lectures and 190 other oral presentations were presented in four parallel sessions. Paralleling the lectures, about 1050 posters were displayed in the lower floor of the Convention Center. Contributions were distributed into fourteen topic areas, with platinum group metals (pgms) featuring in most of these sessions as they retain their pivotal roles in subjects related to sustainable chemistry, most notably in automotive emissions control, hydrogen production, fuel cell catalysis and selective oxidation. Only the presentations relevant to the pgms will be discussed in this review. The EuropaCat 2009 website (1) presents the abstracts of the lectures, oral and poster presentations and other details. In the following, the number under which each lecture appears in the programme is shown in square brackets.

## **The Michel Boudart Award**

The Michel Boudart Award for the Advancement of Catalysis is sponsored by the Haldor Topsøe company,

and is administered jointly by the North American Catalysis Society (NACS) and EFCATS. The recipient is requested to give plenary lectures at the biennial EuropaCat conference series. The award recognises and encourages individual contributions to the understanding of the mechanisms and active sites involved in catalytic phenomena and to the development of new methods or concepts that advance the understanding or practice of heterogeneous catalysis.

Professor Avelino Corma (Instituto de Tecnología Química, Valencia, Spain) received this year's Michel Boudart Award. His plenary lecture [PL-3] covered new mono- and multi-functional catalysts for reactions including oxidation and hydrogenation, leading to new catalytic routes which are more environmentally sustainable. For example, gold nanoparticles supported on titania or ferric oxide catalyse the chemoselective hydrogenation of functionalised nitroarenes with H<sub>2</sub> under mild conditions (120°C, 10–20 atm), avoiding the accumulation of hydroxylamines and their potential exothermic decomposition (2). Corma also showed that Au nanoparticles supported on TiO<sub>2</sub> and nanoparticulate ceria catalyse the aerobic oxidation of aromatic anilines to aromatic azo compounds with yields above 98% under mild conditions. Au on TiO<sub>2</sub> can also act as a reductive catalyst to access the compound directly from nitroaromatics through a two-step, one-pot reaction (3).

### Catalysis by Design Fundamentals

How and why size matters in catalysis was the subject of the plenary lecture by Professor Enrique Iglesia (University of California, Berkeley, USA) [PL-1]. The size and shape of metal clusters determine the degree of coordinative unsaturation of atoms at reactive surfaces. The presence of atoms with low coordination, prevalent on small clusters, lead to stable transition states and surfaces that are more reactive towards the cleavage of chemical bonds during activation of alkanes. Such atoms can also stabilise reactants, such as chemisorbed oxygen atoms, and make them less reactive when used to abstract hydrogen atoms in kinetically-relevant carbon–hydrogen bond activation steps. In this context, Iglesia showed the influence of reactive oxygen atoms during methane conversion on pgm clusters. The use of oxygen as the co-reactant leads to higher rates than with water or carbon dioxide. He provided mechanistic evidence for the reaction of methane with oxygen on platinum, palladium,

rhodium and ruthenium clusters by combining kinetic and isotopic data with density functional theory (DFT). Oxygen forms chemisorbed oxygen atom species as oxygen atom pairs or oxygen atom–vacancy site pairs that activate C–H bonds. Large (8.5 nm) Pt clusters had an O<sub>2</sub> exchange rate constant that is approximately three times higher than small (1.8 nm) Pt clusters, a trend reflecting the weakening of oxygen atom–platinum bond strength and an increase in the basicity of adsorbed oxygen species with increasing cluster size. However, on Pd, Rh and Ru the reaction between CH<sub>4</sub> and O<sub>2</sub> proceeded almost exclusively on surfaces saturated with adsorbed oxygen, because oxygen strongly binds to these metals leading to a lower concentration of vacancies formed at any given O<sub>2</sub>:CH<sub>4</sub> ratio relative to those formed on Pt. Oxygen atom–vacancy site pairs only become available on Pd, Rh and Ru at a much higher temperature or at lower O<sub>2</sub>:CH<sub>4</sub> ratios. Results on iridium clusters were also shown (4).

### Selective Chemical Transformations

Other promising catalysts with well-defined active structures that enable selective chemical transformations were also presented. Marc Armbrüster (Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany) [O1-2] described work that demonstrated the high selectivity of palladium–gallium intermetallic compounds, synthesised in nanoparticulate form and supported on alumina, for the selective hydrogenation of ethyne in an ethene-rich feed. The activity of the nanoparticles was enhanced by a factor of 10<sup>4</sup> to 10<sup>5</sup> compared to Pd–Ga intermetallic compounds in ground powder form and their selectivity was greater than that of the highly active but unselective commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

The selectivity of transition metal catalysts and its optimisation by modifications such as alloying are not yet well understood. Two examples of such effects were shown by Philippe Sautet (Ecole Normale Supérieure de Lyon (ENS), France) [O1-11]. The first example given was the selective hydrogenation of unsaturated aldehydes on Pt-based catalysts, in which the selectivity was shown to be linked with the desorption step of the partially hydrogenated products, a process which can be tuned by alloying platinum with tin. The second illustration dealt with the selective hydrogenation of alkynes on Pd catalysts. *In situ* X-ray photoelectron spectroscopy (XPS) showed that

a carbide-like PdC surface phase was formed during alkyne hydrogenation, but not during alkene hydrogenation, and that this PdC surface phase had a strong influence on the hydrogenation activity and selectivity towards the alkene product. Johannes H. Bitter (Universiteit Utrecht, The Netherlands) and coworkers [O2-3] showed that close contact between Pt and Sn is essential for high selectivity in the hydrogenation of cinnamaldehyde to cinnamyl alcohol over a Sn-promoted Pt catalyst. Close contact could be achieved by using reductive deposition precipitation for the preparation of the catalysts.

There is growing interest in the synthesis of optically pure chiral substances, especially in the pharmaceutical, agrochemical and perfume industries. Among many strategies established for this purpose, enantio-differentiating hydrogenation over a heterogeneous catalyst is one of the most promising methods. Xueying Chen and colleagues (Fudan University, China) [O10-20] replicated the mesostructures of hard silica templates (SBA-15 or KIT-6) to obtain nanostructured Pd catalysts with either a hexagonal or a gyroidal structure. The resulting nanostructured Pd catalysts exhibit superior chemoselectivity and enantioselectivity in liquid-phase acetophenone hydrogenation with the aid of (*S*)-proline.

Xiaolei Fan (University of Bath, UK) [O14-1] discussed work in which microspherical carbon-supported Pt and Pd catalysts were used to demonstrate the feasibility and versatility of a compact flow reactor for different practical applications. The new compact reactor combines the functions of mixing, heat transfer and reaction and allows the use of heterogeneous catalysts prepared by conventional methods. The spherical morphology of the catalyst is essential for application in millimetre-scale reactors. Kinetic results for Heck C–C coupling and alkene hydrogenation catalysed by Pd/C were presented.

### Biofuels and Chemicals

Hydrogenation in the aqueous phase finds extensive application in biofuel production. Such applications include production of alkanes from carbohydrates, ethanol from fermentation products and gasoline from pyrolysis oils. Hakan Olcay (University of Massachusetts Amherst, USA) and coworkers [O2-1] tested several late transition metal catalysts (Ru, Rh, Pd and Pt on activated carbon, Ir on silica, Raney nickel and Raney copper) for aqueous-phase hydrogenation of acetic acid to ethanol in a continuous-

flow packed-bed reactor at 100–260°C and 750 psi. The catalytic activity decreased in the order:



The ethanol selectivity of Ru was the highest of all the catalysts, exceeding 80% at temperatures below 175°C.

In the area of production of chemicals from biomass, Mingyuan Zheng (State Key Laboratory of Catalysis, Chinese Academy of Sciences, Dalian, China) [O6-9] presented work which showed the possibility of using supported bimetallic catalysts containing 5 wt% Pt, Pd, Ir, Ru or Ni with 25 wt% tungsten to produce ethylene glycol from cellulose. Selectivity to ethylene glycol was above 45% (at 6 MPa H<sub>2</sub> and 245°C) and cellulose conversion was almost 100%. The results indicate a bifunctional mechanism, in which W promotes cellulose degradation and the additional metal promotes hydrogenation of the unsaturated intermediates.

### Emissions Control

#### Three-Way Catalysts

Virtually all automotive exhaust systems currently contain pgm-based catalysts. Three-way catalysts (TWCs) are effective for cleaning automotive exhaust gases when the air:fuel ratio is close to 14.6 (5). Materials possessing high oxygen storage capacity (OSC) are necessary to maintain this ratio in the catalytic converter. Evgenii Kondratenko (Universität Rostock, Germany) [O5-23] presented a study of the OSC characteristics of platinum on ceria/zirconia by using carbon monoxide multi-pulse experiments in the presence and absence of O<sub>2</sub>. When gas-phase O<sub>2</sub> was not present, the lattice oxygen of CeO<sub>2</sub> was responsible for the oxidation of CO to CO<sub>2</sub>. To investigate the effect of adsorbed oxygen species, O<sub>2</sub> and CO mixtures were sequentially pulsed, demonstrating that the rate of CO oxidation is increased in the presence of adsorbed oxygen species. It was concluded that it is necessary to design catalytic surfaces that readily provide oxygen species to produce gaseous CO<sub>2</sub> and reduce surface sites.

One of the reasons for deactivation of a TWC is sintering of the precious metal when the catalyst is exposed to high temperatures (~1100°C). In his excellent talk, Hirohito Hirata (Advanced Material Engineering Division, Toyota Motor Co, Japan) [O10-2] presented an *in situ* observation of the behaviour of Pt nanoparticles on CeO<sub>2</sub>-based supports. Alternating

oxidising/reducing mixtures (20% O<sub>2</sub>/He and 3% H<sub>2</sub>/He, 60 s each) were fed to the catalyst at temperatures between 400°C and 800°C and the particle size was measured continuously using *in situ* time-resolved Turbo X-ray absorption (XAS) spectroscopy and transmission electron microscopy (TEM). It was observed that the Pt particle size increased and decreased reversibly as a function of temperature; this behaviour was attributed to the strong Pt–CeO<sub>2</sub> interaction in Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> and Pt/CeO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>.

### Diesel Oxidation Catalysts

Substitution of fossil fuels by biomass-derived fuels changes the characteristics of exhaust gas, by increasing the content of oxygenated hydrocarbons. In this context, Juha Ahola (University of Oulu, Finland) [O4-9] presented research comparing the performance of diesel oxidation catalysts (DOCs) containing between 0.3 g l<sup>-1</sup> and 4.9 g l<sup>-1</sup> of Pt and/or Pd on similar, durable washcoats supported on a metallic substrate with 400 cells per square inch (400 cspi). Hydrothermally-aged Pt-rich DOCs showed better efficiency for the simultaneous removal of hydrocarbons and aldehydes from simulated exhausts containing ethanol, butanol or acetaldehyde, when compared to Pd catalysts with similar characteristics. Pt-rich catalysts were also more durable in the presence of sulfur or other poisons when exposed to actual exhausts.

### NO<sub>x</sub> Abatement

Rigorous restrictions concerning automotive exhaust gas emissions are expected following the introduction of the Euro 5 and Euro 6 regulations. The use of cleaner fuels such as natural gas can play a part in attaining these targets. The nitric oxide produced during natural gas combustion can be removed by using the fuel, i.e. CH<sub>4</sub>, as reducing agent. This can allow complete reduction of NO at high temperature. However, Marc Salaun (Université Pierre et Marie Curie, France) and coworkers [O5-4] pointed out that below 300°C CH<sub>4</sub> is not effective and alternative reducing agents such as H<sub>2</sub> and CO should be used. They studied nitrogen oxides (NO<sub>x</sub>) abatement at low temperature in a reaction mixture containing (in vol%): 0.25 NO, 0.17 CH<sub>4</sub>, 0.48 O<sub>2</sub>, 9.25 CO<sub>2</sub>, 0.47 CO, 0.34 H<sub>2</sub> and 18 H<sub>2</sub>O. A commercial monolithic catalyst containing (in wt%): 1.4 Pd, 0.05 Rh, 0.09 Pt and 3.07 Ce was used to run experiments at various H<sub>2</sub>:CO ratios. It was observed that increasing the H<sub>2</sub>:CO ratio increased the NO conversion and when the H<sub>2</sub>:CO

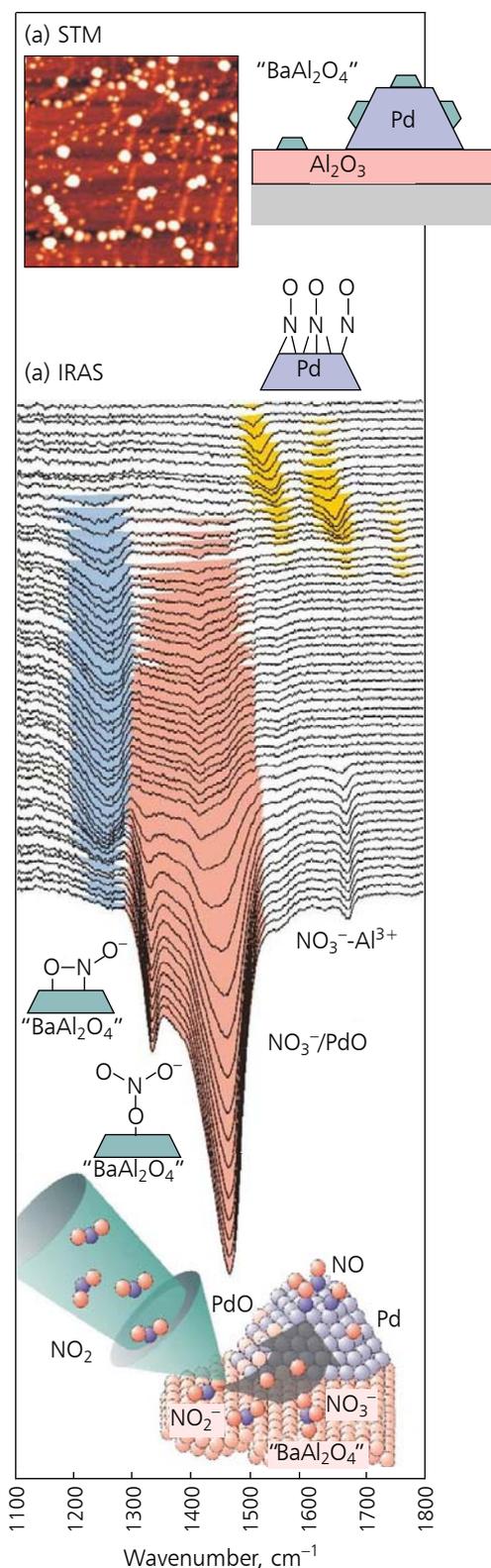
ratio was set at 1.5, total reduction of NO at temperatures as low as 160°C was obtained.

One of the most promising technologies to meet future emissions targets for NO<sub>x</sub> emissions is NO<sub>x</sub> storage and reduction (NSR). An overview of a kinetic modelling approach to NSR operation was presented by Joerg Libuda (Universität Erlangen-Nürnberg, Germany) in a collaborative study with Umicore [O5-1]. A well-defined model catalyst was developed, based on ordered, planar Al<sub>2</sub>O<sub>3</sub> films, on which barium-containing aggregates and the Pd nanoparticles were codeposited. With the help of techniques such as scanning tunneling microscopy (STM), high resolution photoelectron spectroscopy (HR-PES), time-resolved infrared reflection absorption spectroscopy (TR-IRAS) and multi-molecular beam (MB) methods, new mechanistic details were determined for the model system (Figure 1). Frederic Meunier (Université de Caen, France) and coworkers [O11-10] also advanced the understanding of the operation of a commercial NSR material, supplied by Renault, by using *operando* IR spectroscopy. They found that the presence of CO<sub>2</sub> and H<sub>2</sub>O in the feed gas affects the catalytic behaviour of the NSR material. They suggested that the barium carbonates (BaCO<sub>3</sub>) formed over Ba in the presence of gas-phase CO<sub>2</sub> could be partially replaced by nitrates during NO<sub>x</sub> adsorption, accounting for most of the NSR activity.

In real operation, an NSR catalyst works under alternating lean and rich conditions. The NO<sub>x</sub> is adsorbed on a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst when oxygen is in excess (during the lean phase). During the rich phase some reductant is injected, leading to the release and reduction to nitrogen of the previously stored NO<sub>x</sub> species. Atsushi Satsuma (Nagoya University, Japan) [O5-17] presented a Fourier transform infrared (FTIR) spectroscopy study on the effect of various reductants and their concentrations on the nitrate reduction rate and N<sub>2</sub> selectivity of a Pt/K/Al<sub>2</sub>O<sub>3</sub> catalyst. The rate of nitrate reduction by the different reductants follows the order:

hydrogen > propene ~ carbon monoxide > *n*-octane.

N<sub>2</sub> selectivity is dependent on the rate of nitrate reduction independently of the nature of the reductant. For the regeneration step (rich phase), Beñat Pereda-Ayo (Universidad del País Vasco, Spain) [O5-16] presented the results of a study on the optimum combinations of regeneration time and H<sub>2</sub> concentration to achieve efficient operation on a monolithic Pt-BaO/Al<sub>2</sub>O<sub>3</sub>



catalyst. High NO<sub>x</sub> storage capacity (80%) during the lean period and high selectivity to N<sub>2</sub> (90%) during the rich period were obtained.

Selective catalytic reduction (SCR) is an alternative method for the reduction of NO<sub>x</sub> emissions which can be applied to the treatment of industrial flue gas. Angelos Efstathiou (University of Cyprus, Nicosia, Cyprus) and coworkers [O5-5] studied the reduction of NO with H<sub>2</sub> in the presence of excess oxygen over a Pt/MgO-CeO<sub>2</sub> or Pt-Pd/MgO-CeO<sub>2</sub> catalyst, paying special attention to the catalytic performance at low temperature. They illustrated that a combination of Pt and Pd deposited on a nanocrystalline magnesium oxide and ceria carrier led to an N<sub>2</sub> selectivity of between 93% and 100% in the temperature range 120°C to 180°C. They also reported that the addition of 5% H<sub>2</sub>O and 10% CO<sub>2</sub> to the feed gas did not alter conversion or selectivity values.

### Hydrogen Production

Hydrogen production is another interesting field of application of pgms. Steam reforming of methane (natural gas) is the most widespread and generally the most economical way to produce hydrogen, although reforming catalysts still need improvement. Natalia Mezentseva (Boreskov Institute of Catalysis, Novosibirsk, Russia) [O8-5] reported on the development of structured catalysts on heat-conducting metal or cermet substrates (including compressed Ni-Al foam, Fecralloy<sup>®</sup> foil or gauze protected by a corundum layer, and Cr-Al-O microchannel cermets) washcoated with ceria-zirconia fluorite-like mixed oxides and impregnated with up to 1 wt% Pt, Pd or Ru and/or up to 10 wt% Ni. The catalysts were tested in a pilot plant for the autothermal or steam reforming of natural gas, acetone, ethanol, anisole or sunflower oil, showing high and stable performance.

Jens Sehested (Haldor Topsøe A/S, Denmark) and coworkers [O8-6] studied Pt, Pd, Rh, Ir, Ru and Ni impregnated on ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> supports for

Fig. 1. Stages of NO<sub>x</sub> uptake on a NSR model catalyst: (a) STM image of a model catalyst containing barium-based aggregate and palladium nanoparticles co-deposited on an ordered alumina film; (b) TR-IRAS experiment monitoring NO<sub>2</sub> adsorption, dissociation, Pd surface oxidation, surface nitrite and nitrate formation. Colours on the trace identify different species related to the interaction of the nitrate and nitrite molecules with the catalyst. Source: J. Libuda et al., *EuropaCat IX*, 2009

the steam reforming of methane at low oxygen:carbon ratios. Experiments showed that turnover frequency values were proportional to metal dispersion, as can be seen in Figure 2, indicating that the active sites are primarily under-coordinated surface sites, with Rh and Ru being the most active metals, while Pt, Pd, Ir and Ni are significantly less active at equal dispersions.

Joanna Goscińska (Adam Mickiewicz University, Poland) [O8-15] presented a study on Pt catalysts on niobia/zirconia supports as an alternative to Pt/CeO<sub>2</sub> for the water-gas shift reaction. The study concluded that Pt/ZrO<sub>2</sub> is an effective catalyst for water-gas shift and the addition of up to 0.3 parts of niobium relative to zirconium promotes its activity.

Reduction of CO<sub>2</sub> emissions during steam reforming can be accomplished by sorption-enhanced steam reforming (SESR). Li He (Norwegian University of Science and Technology, Norway) [O8-3] discussed the use of Pd/10Ni-30Co/HTL (hydrotalcite-like) catalysts in a dual circulating fluidised bed system, with SESR of glycerol occurring in one bed and regeneration in the other. Without Pd, the catalyst must be reduced in an extra step before being fed to the SESR bed. The presence of Pd allows H<sub>2</sub> to be obtained in 96% to 98% purity with *in situ* reduction of the catalyst.

Michael Bowker (Cardiff University, UK) [O6-3] discussed the possibility of using 0.5% Pd/TiO<sub>2</sub> to photocatalytically convert glycerol, a significant byproduct of biodiesel production, into H<sub>2</sub>. Glycerol first decomposes on the metal surface, producing adsorbed CO

and gaseous H<sub>2</sub>. The adsorbed CO then reacts with O<sup>-</sup> formed when light is absorbed by TiO<sub>2</sub>, forming gas-phase CO<sub>2</sub> and liberating metal sites for further glycerol decomposition. The resulting oxygen vacancies on the support surface are filled by the reduction of H<sub>2</sub>O. Thus, in the presence of light, the reaction is continuous.

### Fuel Cells

Lars J. Pettersson (KTH Royal Institute of Technology, Stockholm, Sweden) in collaboration with researchers at Volvo [O4-10] discussed the successful use of a Pd-based catalyst supported on mixtures of zinc oxide, zinc oxide-alumina and alumina both at the laboratory-scale and in a full-scale reformer, for the autothermal reforming of dimethyl ether (DME) synthesised from renewable sources, at temperatures around 400°C. The system is designed to operate on board DME-fuelled trucks, to provide H<sub>2</sub> for fuel cell auxiliary power units. CO concentration in the H<sub>2</sub> thus generated is low and a water-gas shift purification step catalysed by Pt/CeO<sub>2</sub> further reduces it to only 0.5%, which is suitable for a use in a high-temperature polymer electrolyte membrane (PEM) fuel cell.

Aslihan Sümer (Bogazici University, Istanbul, Turkey) [O8-14] observed that the addition of Pt to Ni/Al<sub>2</sub>O<sub>3</sub> catalysts can produce a catalyst with high activity for the oxidative steam reforming of propane and liquid petroleum gas (LPG), as well as pronounced water-gas shift activity. The optimum Ni:Pt weight ratio was 50. This discovery could be used to simplify the structure of fuel processors to produce

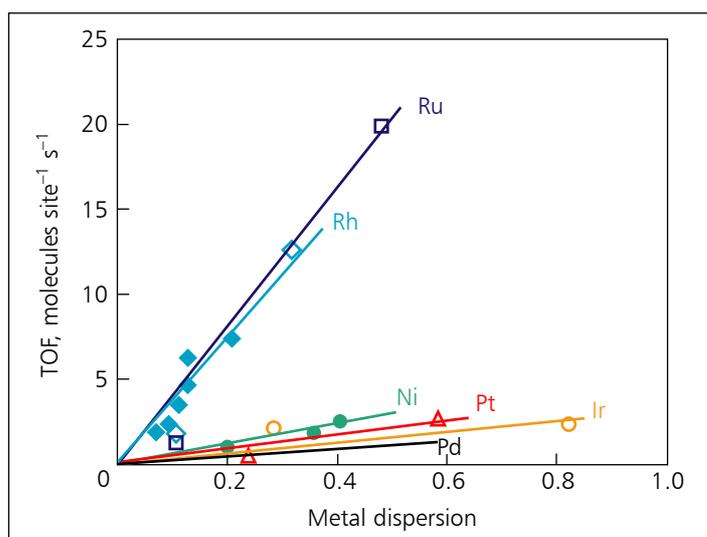


Fig. 2. Reaction rate as a function of metal dispersion for the steam reforming of methane at 500°C in the presence of Pt, Pd, Rh, Ir, Ru or Ni catalysts. Source: J. Sehested et al., *EuropaCat IX*, 2009

H<sub>2</sub> for PEM fuel cells. The observed increase in activity by addition of Pt has been attributed to a decrease in the strength of oxygen adsorption on the Pt/Ni surface.

For normal PEM fuel cell applications, the H<sub>2</sub> feed must contain less than 50 ppm CO. Dimitris Kondarides (University of Patras, Greece) [O8-8] presented a study on the use of selective CO methanation catalysts for the final purification step of reformate gas at low temperature, with suppression of CO<sub>2</sub> methanation and reverse water-gas shift. They tested a combination of several metallic phases (Ru, Rh, Pt and Pd) and catalytic supports (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, yttria-stabilised zirconia (YSZ), CeO<sub>2</sub> and SiO<sub>2</sub>). Long-term stability tests showed that 5 wt% Ru/TiO<sub>2</sub> was very active, selective and stable under realistic reaction conditions and, therefore, was a promising candidate for this application. Addition of up to 30% H<sub>2</sub>O significantly increased the selectivity.

Methane steam reforming can occur internally in a solid oxide fuel cell (SOFC) directly fed with CH<sub>4</sub>. Jamil Toyir (Université Claude Bernard Lyon 1, France) [O8-7] presented an assessment of Ir on gadolinium doped-ceria (CGO) and Ir/Al<sub>2</sub>O<sub>3</sub> catalysts with 0.1 wt% Ir for this application. In spite of the low Ir content, Ir/CGO was found much more active than

Ir/Al<sub>2</sub>O<sub>3</sub>, and no C accumulation was observed even with a large excess of CH<sub>4</sub> relative to H<sub>2</sub>O. The major role of Ir seems to be activation of the CH<sub>4</sub> molecule through methane cracking, which is the rate-limiting step.

### Selective Oxidation

The plenary lecture of Gabriele Centi (Università degli Studi di Messina, Italy) [PL-2] dealt with chemistry, sustainability and innovation as the three key components for the future of society. Professor Centi presented selected results which outlined issues and perspectives on the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> as an example of the challenges involved in the development of more sustainable selective oxidation processes. The reaction is catalysed by Pd and its performance can be improved by doping with either Pt or Au. Selectivity to H<sub>2</sub>O<sub>2</sub> ranges from 80% to 99%, depending on the overall pressure (optimally 100 bar or above), the O<sub>2</sub>:H<sub>2</sub> ratio and the use of solvents which promote oxygen solubility. Table I compares the performance of various pgm-based catalysts in patents selected by Centi (6).

New catalyst formulations for the direct synthesis of H<sub>2</sub>O<sub>2</sub> were also presented by several authors. Salvatore Abate (Università di Messina, Italy) [O3-5]

Table I

Comparison of the Performance of Catalysts from Selected Patents in Direct Hydrogen Peroxide Synthesis

Company	Patent (Year)	Catalyst	H <sub>2</sub> O <sub>2</sub> , wt% (Productivity)	Selectivity, %	Reaction conditions
DuPont	US 4,832,938 (1989)	Pd-Pt (Pt/Pd + Pt = 0.08) colloidal on alumina	19.6	69	136 bar, 5–8°C, 18% H <sub>2</sub> in O <sub>2</sub> , aqueous acid solution (0.1 N HCl)
ENI SpA	US 6,649,140 (2003)	1% Pd-0.1% Pt on carbon	7.3	74	100 bar, 8°C, (autoclave, after 600 h), 3.6% H <sub>2</sub> , 11% O <sub>2</sub> in inert gas, 95:5 methanol:H <sub>2</sub> O solution (+ additives)
BASF	US 6,375,920 (2002)	Pd on monolith	7.0	84	144 bar, 10% H <sub>2</sub> in O <sub>2</sub> , methanol (+ additives)
Hydrocarbon Technologies, Inc	US 6,168,775 (2001)	Pd (-Pt) on carbon black (140 m <sup>2</sup> g <sup>-1</sup> )	9.1 (276 g/g Pd h)	99	~120 bar, ~35°C, (autoclave, after 600 h), 3% H <sub>2</sub> in air, solvent and additives not indicated
Degussa	US 7,005,528 (2006)	2.5% Pd-Au (95:5) on α-alumina	5.1 (13.8 g/g Pd h)	72	50 bar, 25°C (trickle bed), 3% H <sub>2</sub> , 20% O <sub>2</sub> , methanol (+ additives)

showed that H<sub>2</sub>O<sub>2</sub> could be produced with high activity and selectivity at room temperature, using 1 wt% Pd nanoparticles supported on nitrogen-doped multi-walled carbon nanotubes (N-CNTs) in methanol with CO<sub>2</sub> bubbled through it to reach 6.5 bar pressure. The researchers found that the presence of nitrogen functionalities on carbon materials improved the yield of the process and gave a uniform assembly of metal nanoparticles on the CNT surface.

Jennifer Edwards (Cardiff University, UK) and coworkers [O3-6] prepared a series of Au, Pd and Au-Pd catalysts on TiO<sub>2</sub> and activated carbon supports. They found that pretreatment of the supports prior to the impregnation of Au or Pd increased the activity of the catalyst in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. The catalysts were fully stable and reusable without any significant loss of catalyst performance. The addition of acid and halide into the reaction medium promoted catalyst activity when the Au-Pd nanocrystals were present as core-shell structures; however, this effect was not seen for homogeneous Au-Pd alloys., Laura Torrente-Murciano (Imperial College, London, UK) [O3-7] explored the *in situ* synthesis of hydrogen peroxide during selective oxidation of salicylic alcohol to salicylaldehyde using Au-Pd/TiO<sub>2</sub> nanotubes. The reaction showed 100% selectivity to salicylaldehyde, with higher activity than Au-Pd catalysts on conventional supports with air as oxidant.

### Electrochemical Promotion of Catalysis

The pgms can be applied as electrodes for the electrochemical promotion of catalysis. Stamatios Souentie (University of Patras, Greece) [O9-1] discussed the effect of anodic current on an electrochemically-promoted monolithic reactor equipped with twenty-two Rh/YSZ/Pt-type electrocatalytic elements for the reduction of NO by ethene under mildly oxidising conditions at 300°C. A significant increase in NO reduction and CO<sub>2</sub> formation was observed, with NO conversion up to 95% and C<sub>2</sub>H<sub>4</sub> conversion up to 100%. Evangelos I. Papaioannou (University of Patras, Greece) [O13-3] presented a similar study in which the monolithic reactor was equipped with either Rh/YSZ/Pt or Cu/TiO<sub>2</sub>/YSZ/Au cells to carry out the reduction of CO<sub>2</sub>. Using the Rh/YSZ/Pt cells, the conversion to CO<sub>2</sub> reached 5% at 380°C, and using the Cu/TiO<sub>2</sub>/YSZ/Au cells, the conversion to CO<sub>2</sub> was 40%.

Philippe Vernoux (Université Claude Bernard Lyon 1, France) [O9-2] discussed CO oxidation on Pt/YSZ/Pt electrocatalytic elements. An increase in

CO conversion was observed when negative currents were applied, while CO conversion strongly decreased with positive currents. This was attributed to the presence of ionic oxygen species strongly adsorbed on Pt.

### Conclusion

The vitality, breadth and success of research, development and innovation in pgm-based 'catalysis for a sustainable world' were well demonstrated at EuropaCat IX. In general, research and development in catalysis is currently focused on improving selectivity and durability through a better understanding of how catalysts work at the nanoscale. The principles of chemistry relating to interaction between reactants, catalyst and products can be used to successfully design process-specific catalysts. Understanding multifunctional and concerted catalysis, the interaction between sites and the location of active sites within the catalyst is key to the development of more active, selective and durable catalysts for a new generation of cleaner, more efficient processes.

Only oral presentations have been reviewed here, which together with more than a thousand high-quality poster presentations generated occasionally somewhat heated discussion, both in and out of the conference venue. The pgms retain their fundamental role in many topic areas of catalysis and will continue to be the focus of considerable research activity for the foreseeable future.

The next conference in the series, EuropaCat X: 'Across the Disciplines', will be held in Glasgow, Scotland, from 28th August to 2nd September 2011 (7).

### References

- 1 EuropaCat IX: <http://www.europacat2009.eu/> (Accessed on 27th January 2010)
- 2 A. Corma and P. Serna, *Science*, 2006, **313**, (5785), 332
- 3 A. Gorrane, A. Corma and H. García, *Science*, 2008, **322**, (5908), 1661
- 4 J. Wei and E. Iglesia, *Angew. Chem. Int. Ed.*, 2004, **43**, (28), 3685
- 5 J. T. Kummer, *Prog. Energy Combust. Sci.*, 1980, **6**, (2), 177
- 6 G. Centi and S. Perathoner, *Catal. Today*, 2009, **143**, (1–2), 145
- 7 EuropaCat X: <http://www.europacat.co.uk/> (Accessed on 27th January 2010)

### The Reviewers

---



*Juan R. González-Velasco is Professor of Chemical Engineering in the Faculty of Science and Technology at the University of the Basque Country in Bilbao, Spain. He is the President of the Spanish Society of Catalysis (SECAT) and was the Chairman of the Organising Committee of EuropaCat IX. His research group, 'Chemical Technologies for Environmental Sustainability', addresses the synthesis of pgm and base metal catalysts for chemical reactions relevant to energy conversion and for prevention or remediation of negative environmental impacts for cleaner chemical production.*



*M. Pilar González-Marcos is an Associate Professor of Chemical Engineering in the Faculty of Science and Technology at the University of the Basque Country. She was involved in the Organising Committee of EuropaCat IX. Her main research interests at present are focused on the purification of hydrogen by CO-PROX for PEM fuel cells and the upgrading of polymer wastes to fuels by hydrotreating processes.*



*Beñat Pereda-Ayo received his masters diploma in Chemical Engineering at the University of the Basque Country in 2006. Since then, he has been involved in the study of platinum-containing monolithic catalysts for nitrogen oxides storage and reduction (NSR) in the exhaust gases of lean-burn engines, at the Department of Chemical Engineering of the same university. His research brings together experimental and modelling approaches to elucidate the mechanisms and optimise the operating conditions to achieve the most efficient NSR process.*