

# Conference Reports

## Gold 2006

### Highlights of 4th International Conference on the Science, Technology and Industrial Applications of Gold

Limerick, Ireland

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**Michael Cortie, Antonio Laguna,  
David Thompson**



*Prof Julian Ross, University of Limerick and Dr Christopher Corti, World Gold Council, greet two of the Plenary Keynote speakers, Dr Mary Cahill and Prof Graham Hutchings, at GOLD 2006.*

This stimulating event began on the Sunday afternoon with welcoming addresses by Jim Burton, Chief Executive Officer of World Gold Council, and Vincent Cunnane, Vice-President of Research, University of Limerick. This well attended first session was then addressed by four keynote speakers who introduced the innovative roles of gold catalysts, and indicated their commercial potential and the fascinating areas of gold nanotechnology and materials. The final talk in this opening session, entitled 'Irish Prehistoric Gold' was given by Mary Cahill, The National Museum, Dublin, Ireland. Below, we highlight some of the talks with results likely to lead to new applications for gold in the three principal areas of the conference, i.e. gold catalysis, chemistry and nanotechnology and materials. The material presented in some of the posters is also included. In addition, there was an open forum on how to increase gold catalyst durability and some of the principal comments and suggestions from this discussion session are also indicated here, together with some post-conference thoughts. Altogether there were 303 participants, compared with 90 in Cape Town in 2001 and 205 in Vancouver in 2003, numbers which indicate the increasing interest in the themes of these conferences.

The dramatic recent reappraisal of the catalytic activity of gold was well illustrated via the following limerick presented by Graham Hutchings (University of Cardiff, UK) at the end of the François Gault Lecture, and inspired by the location of the conference:

*There once was a scientist of old  
Who said that "all chemistry's been told"  
Now his soul we will save  
Though he'll turn in his grave  
For now all new chemistry is GOLD*

Graham would award a prize for the best limerick written by a GOLD 2006 participant during the conference: this prize went to Peter Radcliffe, Rand Refinery, South Africa, for the following:

*The search for novel materials went cold  
What could be cast or wrought or rolled?  
We came to Limerick  
To learn what to pick  
And for industry the answer is gold*

The other prizes are listed at the end of this article.

## 1 Catalysis

***A Golden Future for Green Chemistry (François Gault Lecture)*** Graham Hutchings indicated that gold catalysts have now become a well established best choice for many chemical transformations. It is also at the heart of a number of new developments in green technology since it has been found to be an extremely active and selective oxidation and

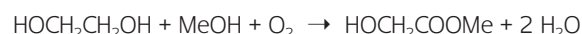
hydrogenation catalyst. The principles of green chemistry include prevention of waste, use of renewable feedstocks, use of catalysts rather than stoichiometric reagents, use of safer solvents and reaction conditions, and increased energy efficiency: catalysis by gold could help in all these areas. There has been a marked increase in rate of growth of interest in catalysis by gold in recent years, as illustrated by the rapid growth in numbers of publications. The opportunities for gold were illustrated using the examples of hydrogen peroxide synthesis and selective oxidation using Au/C and Au-Pd/TiO<sub>2</sub> catalysts.

**Pd-Au Catalysts for the Production of Vinyl Acetate – Review of Patent and Scientific Literature** Hans Lansink Rotgerink, Degussa, Germany, described the well established commercial process for the manufacture of vinyl acetate monomer (VAM) from ethene, acetic acid and oxygen using Au-Pd catalysts (1). This process was developed in the 1960s, has been used commercially since the 1970s and today VAM is produced with high selectivity and high space time yield in many plants around the world. Worldwide VAM capacity is currently ca 5 million metric tonnes per year, and is expanding: 80% of which is produced via the ethene route. VAM catalyst consumption is several hundred tonnes per annum. Potassium acetate is widely used as a co-catalyst and BP have recently introduced a fluidized bed process; the other processes use fixed beds. The increased space time yield now expected requires efficient heat removal. The catalyst is durable and typically lasts for between one and two years. There may be a liquid phase aspect to the process as well as gas phase which may help to increase the catalyst durability.

**Project AuTEK: Gold Research to Industrial Products** Roger Paul, General Manager, Mintek, South Africa, described the joint venture taking place between Mintek (Government funded research) and the three major South African mining houses, AngloGold Ashanti, Gold Fields and Harmony Gold to develop new industrial applications for gold, called Project AuTEK. There are multidisciplinary interactions between AuTEK project members and appropriate universities in South Africa and elsewhere and the results indicate that R&D expertise can be built in South Africa and has the potential to broaden the value added aspects of the local gold industry. Technological fields of interest include the environment, the hydrogen economy, nanotechnology, and biomedical applications. Collaboration with end-users focuses research for specific applications and a semi-commercial gold catalyst production plant has been operated in order to build a commercial catalyst plant in South Africa designed to consume tens of tonnes of gold per annum. Typically a commercial product evolves via basic research and then directed industrial R&D to product research in collaboration with end-users and then product development and market adoption to meet a commercial need. The costs are considerably more in the later stages than the earlier and require significant investment.

**Selective Oxidation of Alcohol to Carboxylic Ester**

**over Supported Nanogold Catalyst** Toshio Hayashi, Nippon Shokubai Co Ltd, Osaka, Japan, described the recently developed liquid-phase air-oxidation process for the one-step direct production of methyl glycolate from ethylene glycol and methanol using a gold catalyst:



A pilot plant demonstration, with a capacity of tons per month successfully demonstrated this can be run as a clean and simple continuous process with the product obtained in high purity. The catalyst used for this reaction in the associated published paper was Au-Pb/Al<sub>2</sub>O<sub>3</sub> (2).

**Higher Active CO Oxidation Catalysts via Physical Vapour Deposition (PVD) – Key Differences between Solution-Derived Nanogold Catalysts and Nanogold by Physical Vapour Methods** Larry Brey, 3M Center, St Paul, MN, USA pointed out that in the 20 years since Prof Haruta's initial dramatic breakthrough on the low temperature oxidation of CO with oxide-supported nanoparticulate gold, and much effort on optimizing solution methods for preparing gold catalysts, a simple reproducible, cost effective method of forming gold nanoparticles and depositing them on a wide variety of substrates to make reproducible highly active oxidation catalysts is proving elusive. 3M have now found that very active gold nanocatalysts can be prepared via PVD (3, 4) on a wide range of supports, including some that are water soluble. The method provides the advantages of low cost, superb reproducibility, removal of the need for washing and thermal treatment steps, and there are no toxicity hazards. It takes only 2 – 3 h to make 400 ml catalyst and there is minimal loss of gold. Such 0.7%Au/TiO<sub>2</sub>/C catalysts are stable for two years if kept in a canister for use in respirators. PROX catalysts of this type have been developed for removal of CO in hydrogen streams down to < 1 ppm (at < 70°C).

**Materials Synthesis and Catalysis of Palladium-Coated Gold Nanoparticles** Michael Wong, Rice University, Houston, Texas, USA, has found that palladium on gold nanoparticles can be 70 times more active than Pd supported on alumina on a per g Pd basis, for the aqueous-phase dehydrochlorination of trichloroethene. This offers a valuable opening to applications in water purification where there is an environmental need to remove harmful chlorinated hydrocarbons.

**Unique Catalytic Properties of Gold for Chemoselective Redox Reactions** Avelino Corma, Universidad Politéchnica de Valencia, Spain, said that the reduced dimensions of nanogold and their interaction with the support are key factors in activating gold from its bulk inert state. However the best catalyst for one reaction is not necessarily the best for another. The particle size of the support may also play a critical role, and nanoparticulate gold can catalyse the chemoselective oxidation of alcohols and aldehydes as well as the reduction of some functional groups using hydrogen as reducing agent. XPS investigations have

indicated the presence of Au<sup>0</sup>, Au<sup>+</sup> and Au<sup>3+</sup> during some of these reactions.

**Immobilized Gold Nanoparticles as Active Alkane Oxidation Catalysts** Ryan Richards, International University Bremen, Germany described use of solvent-free aerobic oxidation of cyclohexane to the nylon intermediates cyclohexanone and cyclohexanol using mesoporous silica SBA-15 and other supports for gold: high TONs and improved selectivities over prior art were achieved.

**Highly Efficient Au/TiO<sub>2</sub> PROX System for Complete Removal of CO in Fuel Cell Systems** Gary Patrick, Project AuTEK, Mintek, Johannesburg, South Africa, described how an unconventional Au/TiO<sub>2</sub> system has been used at room temperature to completely remove CO from hydrogen streams from dry inexpensive impure hydrogen-rich gas which could be used on-board a vehicle. The electrochemical performance of a fuel cell with platinum catalysts was maintained at 100% efficiency using this gold catalyst system.

**Long Term Stability of Au/Al<sub>2</sub>O<sub>3</sub> Catalysts in Continuous Glucose Oxidation** Nadine Thielecke, Federal Agricultural Research Centre, Braunschweig, Germany described how in a continuous reactor the oxidation of glucose to gluconic acid had been maintained at high activity and selectivity for up to 110 days, with catalysts prepared by deposition precipitation and incipient wetness methods. 3.8 tonnes of gluconic acid were obtained per gram of gold. The catalysts were thus shown to have excellent long term stability.

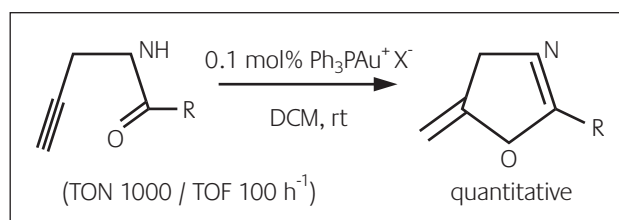
**Evidence of the Active Species in Supported Gold Catalysts** Bruce Gates, University of California, Davis, USA, said that gold that is highly dispersed on oxide supports is highly reactive for reactions such as CO oxidation, the water-gas shift and selective for numerous oxidation reactions. The proposed catalytically active species include zerovalent nanoparticles, with size-dependent properties, isolated cationic gold, gold in nanoparticles at the gold-support interface, and support structures with redox properties. There is evidence that the role of the support is important especially in regard to activation of O<sub>2</sub>. The literature on CO oxidation was critically reviewed with the conclusion that more *in situ* spectroscopic measurements together with measurements of catalyst performance, are needed to determine the reactive species and catalytic intermediates formed from CO and O<sub>2</sub> on the catalyst surface.

**In-situ Transient FTIR and XAS Study of CO Oxidation on Au/TiO<sub>2</sub>** Mayfair Kung, Northwestern University, Evanston, IL, USA, described studies designed to gain insight into the nature of the active site and mechanism for CO oxidation. There was a correlation of CO oxidation activity with degree of reduction of Au<sup>3+</sup> to Au<sup>0</sup>. On an Au/TiO<sub>2</sub> sample activated by reduction in hydrogen at room temperature, and having 2nm Au particles, 0.18 ± 0.03 mol CO/mol Au are adsorbed at -60°C, this giving an IR band at 2090 cm<sup>-1</sup>. While CO adsorption can be readily detected on the sample by FTIR and XANES, it appears that there is only a very small quantity of adsorbed oxygen. Possible evidence

for the formation of an intermediate hydroxycarbonyl was also obtained.

**CO Dissociation and Reaction at Supported Gold Catalysts** Albert Carley, Cardiff University, UK described TAP and XPS investigations used to try and elucidate the mechanism of CO oxidation. A coprecipitated Au/Fe<sub>2</sub>O<sub>3</sub> catalyst was shown in continuous microreactor studies to be active for CO oxidation at 25°C. The catalyst could be deactivated at 100°C in vacuo and reactivated after water treatment. When reactivated using H<sub>2</sub><sup>18</sup>O the CO<sub>2</sub> generated after CO/O<sub>2</sub>/Ar pulses exhibited a time-resolved isotopic distribution indicative of CO bond cleavage. This was pursued by means of XPS measurements on model Fe/Fe<sub>2</sub>O<sub>3</sub>/Au systems in a relatively 'high-pressure' spectrometer: the formation of atomic carbon was clearly observed after exposure of the surface to CO/O<sub>2</sub> mixtures. An analogous ZnO-supported Au model catalyst was unreactive under the same conditions, indicating the importance of a reducible oxide as support.

**Gold Catalysis: News from the Homogeneous Wing** Stephen Hashmi, Universität Stuttgart, Germany described exciting new developments in homogeneous catalysis by gold. Over 50 groups worldwide are working on use of soluble gold catalysts and the number of papers on this topic are increasing rapidly (5). Some reactions, such as phenol synthesis can go smoothly and in high yield with simple homogeneous catalysts such as AuCl<sub>3</sub>. New stereospecific reactions were described using soluble gold catalysts. Some of the reactions described have not yet been achieved using heterogeneous gold catalysts or homogeneous catalysts of other metals. An example where a quantitative yield of product resulted is the following:



**Gold Based Catalyst Performance in Selective Hydrogenation of Diene in an Excess of Alkene**

Antoine Hugon, Université Pierre et Marie Curie, Paris, France, indicated how gold catalysts can be used to selectively hydrogenate diene impurities in the presence of olefins. It is essential to remove these impurities in order to prevent deactivation of the catalysts used for the polymerization of olefins, processes which are operated on a very large scale in industry. A supported gold catalyst made using deposition-precipitation with urea was used to selectively hydrogenate butadiene with high selectivity (>95%) in propene at 100% conversion in the gas phase.

**Deposition of Gold Nanoparticles on Organic Polymers** Masatake Haruta, Tokyo Metropolitan University, Japan, indicated that after catalysts involving nanoparticulate gold on oxides and carbon, gold nanoparticles on polymers

could become important. Gold was deposited on polymers by reducing either tetrachloroauric acid or an ethylenediamine complex with sodium borohydride, trisodium citrate or ethylene glycol. The ease of deposition of nanogold, in other words, Au-polymer interaction, increases in the order PMMA<PE<PVC. It was found that PVP was effective in minimizing the size of Au particles. A 0.5% Au/PVC catalyst with 5 nm Au particles tightly bound catalysed the oxidation of glucose to gluconic acid, but was not active for CO oxidation at 100°C.

**On the Origin of the Catalytic Activity of Gold Nanoparticles** Jens Norskov, Technical University of Denmark, Lyngby, indicated that several effects are contributing to the special catalytic properties of supported gold nanoparticles. The availability of many low-coordinated gold atoms on the small particles is the most important and effects related to the interaction with the support may also contribute, but to a smaller extent. These conclusions were based on a large quantity of experimental data on activities for CO oxidation, and DFT calculations of the effect of metal coordination numbers in comparison with the role of charge transfer, layer thickness and interactions with the support.

**Reactions of Gold Atoms and Small Clusters with CO and CO/O<sub>2</sub>: Matrix Isolation IR Spectroscopic and Theoretical Studies** Qiang Xu, AIST, Osaka, Japan, reviewed the reactions of gold atoms and small clusters with CO and CO/O<sub>2</sub> mixtures using matrix-isolation IR spectroscopy and theoretical calculations as well the related catalytic reactions. Laser-ablated Au atoms co-deposited with CO molecules in solid argon produce mononuclear gold carbonyls at high CO concentration and low laser power, while gold cluster carbonyls are formed with lower CO concentrations and higher laser power.

### More Catalyst Presentations

Altogether there were 61 catalyst talks and 97 catalyst poster presentations and there is insufficient space to summarize all of them in an article of this size. Amongst those with most promise for new applications for gold were 'Direct Synthesis of Hydrogen Peroxide from O<sub>2</sub> and H<sub>2</sub> using Supported Au-Pd Catalysts' by Jennifer Edwards, 'Solvent-Free Oxidation of Alkyl Aromatic Hydrocarbons using Titania-Supported Au-Pd Catalysts' by Dan Enache, and 'New Gold-Containing Catalysts for the Hydrochlorination of Alkynes and Alkenes' by Marco Conte, all from Cardiff, UK. In a presentation entitled 'Single-Phase Gold-Palladium Catalyst: The nature of the Synergistic Effect' Laura Prati (Milan, Italy) described how highly improved catalytic activity in the liquid phase could be attributed to Au-Pd bifunctional sites.

There were a number of talks on PROX catalysts for the purification of hydrogen streams for fuel cells, etc, including 'Study on SiO<sub>2</sub> Supported Au-TiO<sub>2</sub> Nanostructures: The Effect of Preparation Procedure on the Catalytic CO Oxidation in the Presence of Hydrogen' by Anita Horvath (Budapest, Hungary), 'Selective Oxidation of CO in the presence of H<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> over a Gold Catalyst for Fuel Cell Clean-up' by Philip Landon

(Cardiff, UK) and the AuroPureH<sub>2</sub> system mentioned above for purifying 'dirty' dry hydrogen; and also a paper on 'Photocatalytic Methanol Reforming on Au/TiO<sub>2</sub> for Hydrogen Production' by Michael Bowker (Cardiff, UK)

Some papers addressed work relevant to environmental applications. The use of 'Nano-Gold Supported on TiO<sub>2</sub>-Coated Glass Fibre for Removing CO Toxic Gas in Air' was reported by Ben-Zu Wan, Tapei, Taiwan and 'CO Oxidation over Au/TiO<sub>2</sub> under High Space Velocity Conditions for Indoor Air-Quality Control' was the title of the presentation by Hiroaki Sakurai, AIST, Osaka, Japan. Veronique Pitchon, CNRS, Strasbourg, France described gold catalysts with increased resistance to thermal degradation which could be considered for automotive pollution control applications. From work reported by Nikolaos Dimitratos, Milan, Italy in a presentation entitled 'Catalytic Performance of Au Catalysts in the Total Oxidation of VOCs' the best results were obtained with 1%Au/CeO<sub>2</sub> and 1%Au/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalysts.

A large number of presentations discussed the mechanism of gold catalysis, especially CO oxidation but definitive evidence is still awaited (6). For example Jeroen van Bokhoven, Zurich, Switzerland described 'In situ XAS Characterization of the Activation of Oxygen on Gold-Alumina Catalysts', having previously concluded that hydrogen adsorbs dissociatively on Au/Al<sub>2</sub>O<sub>3</sub> (7). From work reported by Shamil Shaikhutdinov, Fritz-Haber Institute, Berlin, in a presentation entitled 'Gold Model Catalysts Supported on Thin Films: Support and Environmental Effects' it was shown that gold restructuring was induced by carbon monoxide and oxygen. There was also clear evidence that impurities in the feedstock (even to the concentrations used in surface science studies, i.e. just a few ppm) may dramatically change the catalyst's surface.

## Round table discussion on how to increase gold catalyst durability

### Industrial Requirements

This was an open forum, chaired by Graham Hutchings (Cardiff University, UK) and David Thompson, and a lively debate ensued. Henrique Teles (BASF, Germany) and Hans Lansink Rotgerink (Degussa, Germany) initiated the discussion by defining the requirements of gas phase chemical processes in industry which include consideration of all the process costs (preparing the catalyst, introducing it into the reactor, the cost of removing it from the reactor, and the costs of disposal and recycling minus the bonus of the recovered precious metal). There should be more than 6 weeks between catalyst regenerations. Resistance to poisons, coking and process disturbances are important, as are strength and attrition resistance over time, particularly for fluidized beds. Catalysts should be stable in storage and one or two years between catalyst exchanges is required: a typical replacement cost for a catalyst is ca 1 million euros, and this should be less than 5% of the variable costs. For liquid phase

processes, a catalyst lifetime of at least a few months is required, and for homogeneous the cost of catalyst recovery is a significant factor. In answer to the question “at what point should academics consider the lifetime of catalysts” the reply was “from the very beginning”, and BASF will only consider catalysts for further development which show almost no deactivation in short duration tests of the kind typically carried out in academia. Even if no deactivation occurs in the first few days, the catalyst has still to be proved to be stable enough over the longer time periods needed for a commercial application. A need for regeneration of catalyst activity leads to recurring additional running costs for the plant.

### Liquid Phase Durability

Ulf Pruesse (FAL, Braunschweig, Germany) reported maintenance of catalyst activity and selectivity over 110 days in a continuous reactor for the oxidation of glucose to gluconic acid in the liquid phase using a 0.3% gold on alumina catalyst, so durability can be achieved for this and maybe other reactions carried out in the liquid phase. This provides encouragement for solving the current difficulties in getting gas phase stability for gold catalysts.

### Room Temperature Considerations

Masatake Haruta (Tokyo Metropolitan University, Japan) indicated the considerations for activity of a catalyst operating at room temperature, e.g. for cleaning living atmospheres: this is a new field for catalysis in general! Deactivation is usual under these conditions (e.g. 30% in one month when stored in glass) due to accumulation of various compounds derived from the atmospheric working environment and most active sites are covered with water, whereas at high temperature catalysts are self-cleaned by heating. Deactivation at room temperature is *not* due to sintering. Au/TiO<sub>2</sub> catalysts used to clean living atmospheres at atmospheric temperatures can be regenerated by photoirradiation for 10 h. Henry Teles said that there is little gain for industry by operating at room temperature, and producing heat at room temperature is a plant design problem, but David Thompson pointed out that this may be the case for chemical processes, but for environmental applications room or low temperature activity is important. In work at Mintek in South Africa, Jason McPherson has confirmed that gold catalysts used for CO oxidation are subject to deactivation in the atmosphere at ambient temperatures; this research has also demonstrated that the presence of CO<sub>2</sub> retards the rate of CO oxidation. DRIFTS has shown formation of carbonates and bicarbonates during catalyst storage in air.

Mike Scurrell (University of Witwatersrand, Johannesburg, South Africa) highlighted the storage of catalyst issues and said that WGS catalyst can change over a short time. Hans Lansink Rotgerink replied that the effect of light and moisture must be considered and why any deterioration is happening. Jack Fletcher (University of Cape Town, South Africa) emphasized the importance of long term on-stream data, and said that initial activity data can be almost useless! Henry

Teles emphasized that catalyst stability is more important than activity.

Mike Scurrell said that it is not yet clear to what extent the research community is aware of the apparent changes which typically take place with gold catalyst in storage. Catalytic properties seem to change (sometimes activity goes up, sometimes down) with storage and influences such as light, temperature, atmosphere play a role. A few papers have given some details but he is concerned about how much reported data is being influenced by the storage effects. If, as seems likely, gold-based catalysts find application in catalytic devices, their ability to survive storage in the device will become very important – decisive even for performance. Encouragement should be given to researching this aspect.

### Mechanistic Thoughts

Bruce Gates (University of California, Davis, USA) pointed out that there are still open questions about the nature of catalytically active species and little about reaction mechanisms has been firmly established; and analogies with homogeneous mechanisms have been used: inferences have been based on observation of likely intermediates and multireaction channels may be operative in CO oxidation. There are only a few reports of catalyst deactivation and long-term catalyst testing is needed for potential applications. There is a need to investigate effects of feed impurities and various products in testing. Aggregation of gold and/or redox processes change activity, and any coke formation is expected to cause deactivation. Characterization of used catalysts would help in understanding the causes of deactivation. There are many different deactivation mechanisms and timescales may vary from hours to years. Catalyst stability needs to be demonstrated and this means long experiment times: somebody must pay, and this is not always realistic for academics. Trace impurities in the feeds can be important and it is better to use real feeds from plants rather than simulated feeds. Geoffrey Bond (Salford, UK) said that the active site must be considered as a basis for determining the mechanism.

Stephen Hashmi (Universität Stuttgart, Germany) has mentioned that in homogeneous catalysis by gold, many organic reactants and products are strong reductants and this leads to *in situ* reduction of gold (gold mirrors, etc). Due to different reduction potentials this seems to be more problematic for Au(III) than for Au(I) catalysts.

### Improved Durability

Improved gas-phase durability can be obtained by insertion of an oxide promoter in the support, or use of a mixed oxide. For example Geoff Bond indicated stability for Au/anatase and Au/SnO<sub>2</sub> for CO oxidation, and uncalcined. Au/FeO<sub>x</sub>-TiO<sub>2</sub> is more stable than when it is calcined. Au/FeCeO<sub>2</sub> is stable for CO oxidation over a period of more than 3 days. Results reported by Ben Nieuwenhuys (Leiden University, The Netherlands) on mixed oxide supports also demonstrate

increased durability for mixed oxide supports, and the support can act as a co-catalyst by providing a source of oxygen.

Donka Andreeva (Sofia, Bulgaria) has indicated that there are two important causes of deactivation of gold catalysts, i.e. formation of carbonate layers and agglomeration of small gold particles. The first cause can be reversed to a significant extent by air/oxygen treatment of the catalysts at low temperature (200 – 250°C), but the second leads to irreversible deactivation. For the improvement of the stability of gold catalysts the following factors are important: choice of support, where a strong metal-support interaction (SMSI) ensures stability of gold particles against agglomeration (TiO<sub>2</sub>, CeO<sub>2</sub>, and in WGS, iron oxide are good examples here). Modification of supports by the addition of a second metal oxide can prevent agglomeration of gold particles. The addition of alumina to ceria increases the stability of gold catalysts in WGS (8). The method of preparation of the ceria-alumina support used in WGS can also be very important, and recently, mechanochemical activation has been shown to be superior to coprecipitation and washcoating for both stability and activity.

### Preparative Aspects

Larry Brey, (3M, Minneapolis, USA) had indicated that there are some applications such as PROX and low temperature CO oxidation for which there are no good alternatives to gold catalysts. The industrial views expressed earlier therefore seemed too pessimistic and a number of research groups are known to be working to improve the stability of gold catalysts. Many practical applications demand a low temperature catalyst. The degree and nature of catalyst stability needed for practical use may differ greatly between, say, a process catalyst for production of vinyl acetate and a CO oxidation catalyst for respiratory protection applications.

The patented 3M physical vapour deposition (PVD) method for preparing catalysts requires no washing of catalyst particles and there are no toxic by-products. It can be used to put nanogold particles on water reactive and water-soluble substrates. It can be used to deposit gold on substrates having any isoelectric point or shape and very little gold is wasted. No heating is necessary to activate the catalyst and an extraordinary degree of reproducibility is attained. Nevertheless some important developments in solution methods for preparing gold catalysts were also reported, including the influence of the final pH and the surface area and type of support chosen.

Anna Maria Venezia (CNR, Palermo, Italy) commented on the noble metal loading of a catalyst: the metal dispersion should be optimised via the preparative method employed: well dispersed systems can match the activity obtained with more heavily loaded catalysts, making the catalysts more economically viable. In answer to the question “what is the best Au loading for industry”, the reply from Henry Teles was “this is not really relevant because it depends on investment versus benefit”, and the loading of the precious metal is only

a problem if the used catalyst is to be thrown away. Chris Corti (WGC, London) pointed out the capital nature of investment in a gold catalyst, because the gold can be recovered.

### Catalyst Testing

Jacob Moulijn (Delft University, The Netherlands) introduced a discussion on standardisation in testing, emphasising the performance principles involved. Robbie Burch (Queen's University, Belfast) said that when publishing results on catalytic activity a reliable benchmark should be included so that everyone can determine just how active (or inactive) a ‘new’ catalyst really is. In water gas shift, many authors claim ‘new’ very active catalysts when in fact they are nothing of the sort. Others claim high activity under model conditions but their catalysts do not perform under more realistic conditions. This all leads to great confusion and time wasting when subsequent authors take the results at face value and plan their work accordingly. On the issue of stability, again there is little consistency in how catalysts are tested, or how the results are reported, so when various people talk about “more stable” catalysts it is hard to know if this has any real meaning. In summary, it was suggested that one message that goes out to researchers is that kinetic measurements should be performed wherever possible using realistic, repeatable, and consistent testing conditions; that activities should not be reported exclusively on fresh catalysts but also at least on repeat experiments with ‘used’ catalysts; and that some sensible reference benchmark be included so that others can see the real activity versus a known standard – the WGC standard catalysts may not be the most active for any particular reaction but providing they give consistent results they can be used to benchmark any equipment in any laboratory. Donka Andreeva supported the idea that a study of kinetics and mechanism could lead to a knowledge of the deactivation processes involved. It was also mentioned (contributor not identified) that it is important to compare selectivities at the same conversion.

Julian Ross (University of Limerick, Ireland) speaking as one of the editors of *Catalysis Today*, pointed out that it is important for those entering a new and emerging field to make sure that the experiments that they plan add something new to the collective pool of knowledge in that area and that their results will be worth reporting. This means that the researcher needs to know the relevant literature inside out and be able to present any new data in the context of the other papers on the same or related subjects; even better, try to find something that has not been done before. In this connection, it is important to stress again the need to provide comparative data to allow the reader to judge fully any new contributions made. Many examples exist in the literature of hot topics that have attracted myriads of researchers, many of whom have produced very repetitive and hence largely uncited work.

For CO oxidation activity, Larry Brey (3M) has studied the effect of feed dewpoint on sputtered Au/TiO<sub>2</sub>/C catalyst:

when the dewpoint is 23°C the CO conversion stays steadily at around 100% over 25 min but when it is <-50°C the percentage CO conversion falls off very rapidly. The WGC reference catalysts perform quite well but not as well as the Au/TiO<sub>2</sub>/C catalyst.

### Final Thoughts

Nina Bogdanchikova (CCMC-UNAM, Mexico) commented that the process of application of scientific discoveries by industry has several stages: (1) discovery of the effect, (2) establishing reproducibility for the results, (3) defining area/conditions/limits where this effect exists, (4) understanding the mechanism of the effect, (5) using the accumulated knowledge to optimize the product or process and (6) successful use by industry. At present we are at stages (3) / (4) but already we can suggest suitable gold catalysts for industrial developments, which can later be substituted by optimized systems.

Henry Teles said that industrialists used to say "There is no short-term test for the long-term behaviour of catalysts". It is unrealistic to ask academia to test catalysts for the long lifetimes required by industry, and often the tests done in academia are far too short. The behaviour of catalysts (particularly heterogeneous) should be followed in a continuous apparatus (and this is much more reliable than using multiple batches) for at least one or two days.

The challenge of the limerick competition initiated by Graham Hutchings in the opening presentation at the conference was responded to by the following contribution by a representative from one of its sponsors, Kobus de Jager (Anglogold Ashanti, Johannesburg):

*I must be bold  
Our gold must be sold  
We must use our learnings to improve our earnings  
The challenge to us all is to play ball  
And meet the collective call*

Dr de Jager added that whatever quantity of gold the scientists are using.....it is too little!

## 2 Chemistry

### **Luminescent Gold-Containing Molecular Materials – From Fundamentals to Functions**

Vivian Wing-Wah Yam, The University of Hong Kong, PR China, described gold complexes having rich luminescence properties, some of them deriving from the strong tendency to form aggregates because of the aurophilic nature of gold. These gold-containing complexes can be molecular triplet emitters. Different approaches and assembly motifs have been employed to tune the absorption and emission characteristics of these materials depending on their spectroscopic origins. Through rational design and synthetic strategies, these molecular materials may find application as

triplet light-emitting materials for OLEDs and chemosensors.

**New Gold Chemistry with Nitrogen Ligands** John Fackler Jr, Texas A&M University, USA, described the synthesis of an important number of stable gold compounds with nitrogen ligands. The chemistry of gold(I) with N-donor ligands is sparse, but he showed how rich it can be when the ligands have delocalized  $\pi$ -networks (amidinate, pyrazolate, carbenate derivatives). Some of them have excellent optical properties or can be used as catalyst precursors for CO oxidation.

**Coordination Polymers with Cyanurate Building Blocks as Advanced Materials** Daniel Leznoff, Simon Fraser University, Burnaby, Canada was focused on supramolecular structures obtained by interaction of dicyanoaurate(I) or tetracyanoaurate(III) salts with other metal centres and described how attractive aurophilic interactions are used to increase the dimensionality in systems containing other metals in addition to Au(I). They also increase thermal stability of [Au(CN)<sub>2</sub>]-based polymers, as is evident in the M(pyrazine) [Au(CN)<sub>2</sub>]<sub>2</sub> system, which for M = Ni can be heated to over 400°C without decomposition. This talk surveyed a range of [Au(CN)<sub>2</sub>]-based high-dimensionality-augmented structures and their physical properties which give them potential as commercial products. The incorporation of cyanaurates as components of advanced materials would provide a new utility and market for these key compounds of the gold mining and refining industry and represent a potential new industrial application for gold.

### More Chemistry Presentations

There were 3 keynotes, 19 oral and 20 poster presentations in the Chemistry Section. The topics were focused on the synthesis of new compounds; some of these of interest, not only from the theoretical or structural point of view, but also for their potential new commercial applications. The chemistry programme was structured in six sessions: 'Organometallic and Coordination Chemistry', 'Metal-Metal Interactions in Macromolecules', 'Physical Chemistry and Recovery', 'New Gold Chemistry', 'Medical and Biological Applications' and 'Luminescence: Science and Applications'.

One of Daniel Leznoff's coworkers, Michael Katz described 'The use of diamagnetic metal nodes with [Au(CN)<sub>2</sub>]<sup>-</sup> linkers for optical materials' whilst Julie Lefebvre presented 'Vapochromic and Magnetic Behaviour of Dicyanoaurate-Containing Coordination Polymers', and these provided some useful and potentially commercially applicable physical properties for this type of macromolecules, such as optical, vapochromic or magnetic materials.

Some details of luminescent biscyclometallated gold(III) alkynyl complexes were presented by one of Vivian Yam's students in the poster 'Luminescent gold(III) alkynyl complexes. Synthesis, Structural Characterization and Luminescent Properties'.

A beautiful chemistry was presented in Symposium 4. William F. Gabrielli, University of Stellenbosch, South Africa, in

his talk 'Utilisation of Various Bonding Modes of N-Rich Heterocycles in Gold(I) Chemistry' described an interesting gold(II) complex without any bridging ligand between the two gold centres. Maria Agostina Cinellu, University of Sassari, Italy, in a talk entitled 'Synthesis and Properties of Gold Alkene Complexes' described the synthesis and chemical behaviour of an important number of olefin gold complexes, which are poorly represented in the chemistry of this metal. Fabian Mohr, University of Zaragoza, Spain, analysed the preparation of some water-soluble gold derivatives in the oxidation states I, II and III.

The theoretical aspects and the influence of the relativistic effects of gold chemistry were analysed by Pekka Pyykko, University of Helsinki, Finland, in his talk 'Ab Initio Calculations on New Gold Compounds' and Miguel Monge, University of La Rioja, Spain, in his talk 'Theoretical Calculations on Au(I)-M(I) (M = Ag, Cu and Tl) Compounds: Metallophilic Interactions and Photophysical Properties' provided a useful practical application in the case of heterometallic derivatives.

It is well known that some polynuclear systems have luminescent properties and these were analysed in a number of talks: Jose M. Lopez de Luzuriaga, University of La Rioja, Spain, in 'Pyridine and Polypyridine Gold Complexes. An emerging class of luminescent materials' showed how the electronic characteristics of the substituents in the pyridine ligand or the presence of metal-metal interactions can affect the energy of the emissions. One of his students, Raquel C. Puelles was nominated by the Chemistry Committee for the best poster presentation by a student for 'Perfluorocarboxylate-silver(I) and aryl-gold(I) as precursors of high nuclearity mixed complexes. M. Concepcion Gimeno, University of Zaragoza, in 'Luminescent Heteropolynuclear Complexes with Chalcogenide and Chalcogenolate ligands' described the synthesis of heteropolynuclear complexes by using difunctional ligands, such as phosphinepyridines. The preparation of luminescent gold complexes with amino-, pyridyl- and picolyl-substituted imidazolium-based ligands was described by Vincent J Catalano, University of Nevada, USA., in his talk entitled 'Luminescent Gold(I) Coordination Polymers Constructed with N-Heterocyclic Carbene Ligands'. Antonio Laguna, University of Zaragoza, Spain described the strongly luminescent heteropolynuclear complexes obtained by reaction between basic gold precursors and acid thallium or bismuth salts in his talk 'Heteropolynuclear Gold Complexes. A strategy for Luminescence'. In many of the compounds described in these four talks, the change of colour and luminescent properties are due to charge transfer from the ligand to the metal centres and can also be influenced by the strength of the metal-metal interactions.

Symposium 26 was entirely devoted to the medical and biological applications of gold compounds and they were analysed in four different talks. In the first one, Zolisa A Sam, Project AuTEK, University of the Free State, South Africa, offered a general view of the compounds used in cryotherapy and, in particular, auranofin analogues,

cyclodextrins and ferrocenyl phosphine derivatives, in her talk 'Coordination Chemistry and Substitution Behaviour of Gold(I) Complexes'. Frankline K. Keter, Project AuTEK, University of Johannesburg, South Africa, in the talk 'Gold Pyrazole Complexes: Synthesis, Characterisation and Kinetics. Comparative studies with platinum and palladium analogues' analysed the chemical behaviour and kinetics of pyrazolyl gold(III) complexes in biological buffers. The talk by Judy Caddy, Project AuTEK, Mintek and University of Witwatersrand, South Africa entitled 'Gold(I) Phosphine Complexes Incorporating Alkyl Substituents with Ethane and Ethylene Backbones' was focused on the use of butylphenyldiphosphines as ligands. An extension of this work to other diphosphine, thioguanine or cis-enkephalin derivatives was presented in three posters. Edward R T Tiekink, University of Texas at San Antonio, USA indicated the use of colloidal gold, e.g. 'Tyndal's purple' as antiarthritic, in his talk entitled 'Nanogoldpharmaceutics: The Use of Colloidal Gold to Treat Experimentally-Induced Arthritis in Rat Models'.

Finally, other aspects such as the electrochemical studies of gold surfaces or the recovery of gold using hydrous iron(III) or supercritical carbon dioxide was analysed in Symposium 12 by Louise M Kinsella, University College Cork, Ireland, Kotaro Yonezu (Engineering, Kyushu University, Japan) and Jeremy D Glennon, University College Cork, Ireland.

### 3 Nanotechnology and Materials

**Nanoparticle Plasmonics of Gold in Active Media** Nabil Lawandy, Solaris Nanosciences, Rhode Island, USA, in his plenary keynote talk discussed the response of gold nanoparticles within active media such as liquid crystals, absorbing solar cell materials and media capable of amplification. The potential uses of gold nanostructures in enhanced display devices, solar cells, and bio-assays were described. In some of these instances the gold particle, often a rod, behaves like a nano-antenna.

**Gold Nanoparticles; a Story of Eternal Return** Mathias Brust, University of Liverpool, UK, indicated that documents in Sanskrit give evidence for the use of gold nanoparticles in ayurvedic medicine some 5000 years ago, but today we are still discussing if and how recent advances in the technology of colloidal gold will present exciting new opportunities for biomedical applications. He was the pioneer of what is now termed the 'Brust method' for synthesis of very uniformly sized gold nanoparticles, and gave an interesting account of the diverse properties of gold nanoparticles, and particularly emphasised their existing and potential biomedical applications. This emphasis found support in the talks of others too. Günter Schmid of University of Duisberg-Essen, Germany, who is the pioneer of methods to produce Au<sub>55</sub> clusters, showed data suggesting that a particular Au<sub>55</sub>-based cluster might have anti-cancer possibilities.

### **Developing Tumour-Targeted Multifunctional Nanotherapeutics using a Colloidal Gold Nanoparticle Platform**

Giulio Paciotti of CytImmune Sciences Inc, Rockville, MD, USA, described how his company has developed a technology to target tumours with gold nanoparticles that carry a payload of tumour necrosis factor (TNF), with very promising results. Successful pre-clinical proof-of-concept nanotherapeutics not only supports further clinical development of these drugs, but also supports the development of additional targeted nanotherapeutics on the pegylated colloidal nanoparticle platform.

**Shape Memory Phase Transformations in the Au-Al-Cu Alloy System** Michael Cortie, University of Technology Sydney, Australia said that shape memory alloys (SMAs) are able to undergo a 'one-way' or 'two-way' (reversible) shape change as a function of temperature. During cooling the shape change begins at the martensite start temperature,  $M_s$ , whereas during heating it begins at the austenite start temperature,  $A_s$ . Alloys in which  $M_s$  and  $A_s$  are within the range 0 – 200°C are currently of the greatest technological interest. Au-based SMAs could be commercially viable in high-value, niche applications such as actuating elements in biomedical implants. Shape memory alloys were also described in a poster by Stefano Besseghini of CNR-IENI, Italy.

**Gold Nanorods: Properties and Manipulation** Jorge Pérez-Juste, Universidade de Vigo, Spain described the synthesis of nanorods by means of a modified seeding growth method which is easily tuned in its aspect ratio from 1 to 5. Methods for obtaining larger systems which retain the optical properties of the original nanoparticles were indicated, as well as for manipulation through preferential orientation or selective melting.

## **More nanotechnology and materials presentations**

Getting the gold nanoparticle to the desired site is of course very important for the medical applications, and various types of surface modification of the particle are being explored, a topic addressed by Robert Tshikudho, formerly of University of Liverpool and now at Mintek, South Africa. Mpfunzeni Raphulu and Daven Compton, also of Mintek, have synthesized gold-polymer composites prepared by *in situ* reduction of  $\text{HAuCl}_4$ , and an electrospinning technique was used to make interwoven nanofibres having embedded gold nanoparticles. Diagnostic application of gold nanoparticles is a more mature field but obviously still bursting with opportunity. One of the talks in this area was that of James Carney of British Biocell International, who described how the aggregation of gold nanoparticles is being further developed to make portable and ultrasensitive medical diagnostic kits. Several other talks explained how gold nanoparticles, sponges or surfaces could be exploited to offer biosensing, analytical or diagnostic platforms.

However, the potential or existing applications of gold are not confined to biotechnology. Michael Cortie as well as Nabil Lawandy (see above) were among those who presented talks showing other technological possibilities for gold nanoparticles, in particular for display devices and spectrally-selective coatings. And, of course, gold nanoparticle-based inks and glazes are a commercially significant and growing activity, as exemplified by a talk of Peter Bishop of Johnson Matthey Technology Centre, UK. In all of these instances the high value of gold is not an impediment to its use since only small quantities are used.

The more fundamental end of science was also represented. Mike Ford of University of Technology Sydney, and Ignacio Garzón of University Nacional Autonoma de Mexico explored the structure and physical properties of naked gold clusters, primarily by using *ab initio* computational techniques since naked clusters of small size present intractable experimental difficulties for direct study. A real showstopper was a talk by Maik Eichelbaum of Humboldt-Universität zu Berlin, who described how such tiny clusters of Au atoms exhibited unusual luminescent optical properties. But the slickest presentation of all may have been that of Toshiharu Teranashi of University of Tsukuba, Japan, who gave an interesting talk on thiolated gold clusters, and this generated much interest from the floor.

In other presentations, more focused on materials science, there was one by Takanobu Shiraishi, of Nagasaki University, Japan on the colours of gold alloys for dental use, while the wonderful intermetallic compound 'purple gold', or 'purple glory' ( $\text{AuAl}_2$ ) was addressed at least twice, first by Kate Wongpreedee from Srinakhariwrot University, Thailand, who showed how it can be cast and shaped into jewellery items, as well as by Michael Cortie et al, who focused instead on the potential applications of the mesoporous gold sponge left behind when the  $\text{AuAl}_2$  is de-alloyed. Stefania Ferrara of RWTH Aachen University, Germany, gave an interesting account of 'active metal solders' based on Au and reactive elements such as titanium. These allow bonding of some seemingly improbable pairs of materials such as titanium alloys to  $\text{Al}_2\text{O}_3$ , and are becoming of increasing value in high tech industries such as aerospace. Jörg Fischer-Bühner of Forschungsinstitut Edelmetalle & Metallchemie (FEM) described how the process of equal channel angular pressing (ECAP) can be used to impart an unprecedented combination of strength and hardness to pure Au. Other interesting properties can be obtained by surface alloying gold with nitrogen, as described by Lidija Siller of University of Newcastle upon Tyne, UK. An interesting electroforming technology for gold was described by Antonello Vincenzo of Politecnico di Milano, Italy. There were also many other excellent and interesting presentations in both the nanotechnology and the materials sessions which we cannot mention here due to lack of space.

## 4 Conclusions

Overall, GOLD 2006 had resulted in getting together an effective concentration of researchers with an interest in gold catalysis, chemistry, nanotechnology and materials science, and there are many potential new applications for gold in all topic areas represented by the conference.

Prizes for presentations at the conference were awarded as follows:

*Best Catalysis oral [Anglogold-Ashanti prize]:* Tatsuya Tsukuda, Institute for Molecular Science, Okazaki, Japan for 'Polymer-stabilized gold clusters as quasi-homogeneous catalysts for aerobic oxidation of water'

*Best Chemistry oral [Harmony prize]:* William Gabrielli, University of Stellenbosch, South Africa for 'Utilisation of various bonding modes of N-rich heterocycles in gold(I) chemistry'

*Best Materials/Nano oral [Gold Fields prize]:* Toshiharu Teranishi, University of Tsukuba, Japan, for 'Large-scale selective synthesis of thiolated Au<sub>25</sub>clusters'

*Best student oral [Rand Refinery prize]:* Julie Lefebvre, Simon-Fraser University, Canada, for 'Vapochromic and magnetic behaviour of dicyanoaurate-containing coordination polymers'

*Best Student poster [WGC prize]:* Stefanie Lim, State University of New York, USA, for 'Gold nanoparticles: mediated assembly towards functional nanostructures'

*'Catalysis by Gold' book prize for best new idea:* Michael Wong, Rice University, Houston, USA, for 'Materials synthesis and catalysis of palladium-coated gold nanoparticles' in which high catalytic activity for Au-Pd nanoparticles was reported for the hydrodechlorination of trichloroethene, a frequently encountered water pollutant.

This summary is aptly concluded by a limerick contributed by Geoff Bond:

*Researchers were formerly told  
There was no point in working with gold;  
But Haruta decreed  
We must get up to speed  
And search for the riches untold!*

We look forward now to the further progress which will be evident in GOLD 2009!

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