

# CatGold NEWS

A newsletter for information exchange on developments and progress in gold catalysis and its applications

The excellent news this issue is that eight European research centres will be funded to work on gold catalysis over the next four years.

The European Commission has approved a sum of €1.5 Million for the AURICAT collaboration and Dr. Adrian Taylor reports on this in this issue. You will no doubt be pleased to hear of progress on the Council's Reference Catalyst Programme and the GOLD 2003 Conference (see the first call for papers contained in this issue). Please submit your paper offers as soon as possible, since we are anticipating a very full programme with attendance from both academics discussing the very latest research results, and industrialists interested in commercially developing the science. Parallel sessions on the associated sciences of gold chemistry and nanotechnology, as well as materials, will also be of interest.

Also in this issue is an article on research on gold catalysis in the USA, by Professor Mayfair Kung of Northwestern University. If you would like to submit an article for the next issue of CatGold News (due early Spring 2003) please contact us at the address on the back page.

## €1.5 Million for AURICAT



A 1.5 million Euro research training network on the topic of **Catalysis by Gold** has recently been funded by the European Commission. The network is led by *Professor Graham J Hutchings* of The University of Wales, Cardiff, UK (Coordinator) and *Dr Adrian O Taylor* of The University of Salford, UK (Deputy Coordinator). They are assisted by *Professor Geoffrey C Bond* (Visiting Professor at Salford) and *Dr David T Thompson* (Consultant to World Gold Council), who act as consultants to the network. The Network is named **AURICAT**.

Contract negotiations are now almost complete, and the funding will pay for a total of some 19 person-years of young post-doctoral researchers time, to enable work in various European Laboratories over the course of the 4-year project. The network involves eight university laboratories, where the post-docs will be based, four major chemical companies, where the post-docs will gain industrial work experience and the World Gold Council.

The wide-ranging project aims to further our understanding of the catalytic activity of gold and includes efforts to discover novel applications for gold catalysts, building in particular on the pioneering efforts of the research groups of Bond, Haruta and Hutchings [see reference 1 for a recent, detailed review]. Early on during the project an AURICAT website will be set up, to enable progress to be followed.

The principal objectives of the AURICAT Network are as follows:

- 1 To train several post-doctoral researchers in the relatively new field of Catalysis by Gold, thus enhancing their career prospects and providing a means for technology transfer.
- 2 The improvement of existing preparation methods for gold catalysts and analysis of the chemistry underlying these methods.
- 3 To study the stability of gold catalysts, including the exploration of methods for limiting catalyst deactivation, for re-activating catalysts and for the recovery of gold from spent catalysts.
- 4 To gain a greater understanding of the mechanism(s) by which gold catalysts operate when used for carbon monoxide oxidation, for the water gas shift and for the selective oxidation of hydrocarbons.
- 5 The development of new gold-based catalysts and advanced formulation methods, with emphasis on the use of different supports and different methods for applying the gold to the supports.
- 6 To discover novel uses for gold catalysts, both heterogeneous and homogeneous (including anchored complexes).

An important element of the methodology to be employed on this project is the complementary input from groups with a wide range of expertise in the fields of Heterogeneous Catalysis, Homogeneous Catalysis, Reaction Engineering and Industrial Catalysis. The network has expertise in process engineering (including scale-up), high throughput and combinatorial testing methods, reaction modelling, supported metal catalysts, microporous solids, organometallic chemistry, surface science and computational chemistry.

In addition to specialist scientific training, all the young post-docs will play a significant part in the management of the network, taking increasing responsibility as the project



GOLD 2003  
NEW INDUSTRIAL USES FOR GOLD

● **GOLD 2003 Conference, Vancouver, September 28 – October 1**

Planning for the GOLD 2003 Conference Sessions on Catalysis is now well underway.

The Catalysis Technical Committee is being chaired by Professor B E Nieuwenhuys, Leiden University, The Netherlands. Its other members include Dr Larry Ito (The Dow Chemical Co.), Dr Joaquim-Henrique Teles (BASF AG), and Professors Jack Fletcher (Cape Town, S Africa), Wayne Goodman (Texas A&M, USA), Graham Hutchings (Cardiff, UK), Yasuhiro Iwasawa (Tokyo, Japan) and Mayfair Kung (Northwestern, USA). Patrons of the conference include Professor Geoffrey Bond (University of Salford, UK), Dr Masatake Haruta (Director, Institute for Green Technology, AIST, Japan), and Professor Hubert Schmidbaur (Technical University of Munich, Germany).

Further details about the conference can be found on the conference website at [www.gold2003.org](http://www.gold2003.org)

Extended abstracts (ca 2 x A4 pages) for proposed papers or posters should be submitted via this conference website.

Questions regarding the conference technical programme should be addressed to:

**Technical Programme Coordinator, GOLD 2003, World Gold Council, 45 Pall Mall, London, SW1Y 5JG, UK.**  
Fax: +44 20 7839 6561  
E-mail: [gold2003@gold.org](mailto:gold2003@gold.org)



Vancouver – the GOLD 2003 venue

● **Fuel Cells Science and Technology 2002, 24-25 September 2002, Amsterdam, The Netherlands**

This Grove Fuel Cell Symposium event contains a poster presentation by Don Cameron of the Interact Consultancy, and Richard Holliday and David Thompson of World Gold Council, entitled 'Gold's Future Role in Fuel Cell Systems'.

## Research on Gold Catalysis in the USA

There has been significant increase in the research activity on gold catalysis in the USA, involving collaborations as well as individual research groups. The group at **Northwestern University** (M Kung and H Kung, DL Johnson, L Marks), in collaboration with J Miller (**BP-Amoco**) is attempting to identify the nature of the active sites on gold catalysts, and to generate a better understanding of the chemistry in the preparation of supported gold catalysts. Experimental support exists for a model of the active site for CO oxidation involving an ensemble consisting of a gold cation-hydroxyl complex with neighbouring gold atoms. They have also identified the role of chloride in poisoning the active sites.

A collaborative project exists between H Kung and M Kung at Northwestern, B Gates at the **University of California, Davis**, R Davis at the **University of Virginia**, A Datye at the **University of New Mexico**, R Lobo at the **University of Delaware**, N Coville and M Scurrill at the **University of Witwatersrand**, and



The research group at Northwestern University with Dr. Jeff Miller from BP

J Fletcher and Eric van Steen at the **University of Cape Town**. The group is studying new methods to synthesize supported gold catalysts, the reaction mechanism for carbon monoxide oxidation, and the effects of modifiers in gold catalysis, including the use of bimetallic catalysts.

Another project headed by S Overbury with others at **Oak Ridge National Laboratory** and M Amiridis at the **University of South Carolina**, focuses on ordered mesoporous supports to synthesize and stabilize monodispersed Au nanoparticles for CO oxidation and VOC destruction. Amiridis is also studying the synthesis of supported bimetallic PtAu nanoparticles of controlled structure and composition, using organometallic bimetallic precursors with the desired metal-metal bonds. His group also explores the synthesis of bimetallic PtAu nanoparticles in solution utilizing dendrimers as 'hosts' and the subsequent anchoring of these particles on inorganic supports. These catalysts are to be evaluated for partial oxidation and selective reduction of NO<sub>x</sub> by hydrocarbons.

At **Purdue University**, WN Delgass, R Andres, and J Lauterbach are engaged on the fundamental mechanisms governing production of propylene oxide from propene, oxygen and hydrogen over Ti-modified gold catalysts. A combination of spectroscopic characterization, unique materials synthesis, and kinetic analysis is used to probe the active sites and the role of hydrogen. K Thomson and WN Delgass are engaged in research on gold cluster reactivity. Modern DFT simulations are being used to study dissociative adsorption of oxygen on gold to rationalize reactivity dependence on cluster size and

spin state. At **Texas A&M University**, DW Goodman's group is investigating gold clusters of approximately two atoms thick and thus resembling rafts on the oxide support. The electronic properties of these particles are between those of atomic gold and bulk gold and thus uniquely characteristic of the nanoscale. They found that if gold clusters maintain their unique shape and size, the partial oxidation of propylene to propylene oxide in the presence of oxygen takes place. However, gold is a highly mobile element on these surfaces and the gold rafts rapidly coalesce into larger particles and lose their special selectivity for making propylene oxide.

J Regalbuto at the **University of Illinois, Chicago**, in collaboration with J Miller (BP-Amoco), is investigating the fundamental processes that occur when gold coordination complexes such as tetrachloroaurate adsorb onto alumina. Their study includes molecular characterization of the coordination chemistry of dissolved and adsorbed complexes using EXAFS, and the measurement of gold uptake and

adsorption kinetics as functions of pH, ionic strength, and other parameters pertinent to catalyst impregnation.

At **Tufts University**, M Flytzani-Stephanopoulos's group is studying Au-CeO<sub>2</sub> with formulations, with high activity and stability in the low temperature (200-300°C) WGS reaction. At the **University of Washington**, C Campbell's group has studied the bonding of oxygen and propene to Au nanoparticles on TiO<sub>2</sub>(110), measuring the sintering kinetics and modelling these with kinetics derived from accurate mechanistic/atomistic models using calorimetric input about how the metal nanoparticle's energy varies with size.

At the **University of Michigan**, L Thompson and his students focus on the use of oxide-supported gold catalysts for the water gas shift reaction with emphasis on developing a fundamental understanding of their high activities and poor stabilities. They are also developing carbide supported gold catalysts. E. Gulari is studying NO<sub>x</sub> reduction and selective CO oxidation over supported Au catalysts. At the **University of Wisconsin**, Madison, M Mavrikakis' group has investigated the effect of strain and steps on the thermochemistry and kinetics of the activation of O<sub>2</sub> on various single crystal gold surfaces by computational chemistry. They showed that both strain and defect sites enhance the reactivity of gold particles, and are currently studying the WGS reaction on gold-based catalysts. ■

**Mayfair Kung** ([m-kung@northwestern.edu](mailto:m-kung@northwestern.edu))

Department of Chemical Engineering, Northwestern University, Evanston, IL 60208-3120, USA

# IPMI Award for Dr Haruta

The 2002 International Precious Metals Institute (IPMI), Henry J Albert Award has been presented to Dr Masatake Haruta. The award was made at the 26th IPMI Conference, Miami, Florida. Sponsored by Engelhard Industries, this award recognises outstanding theoretical and experimental contributions to the science of precious metals. This year's award was presented to Dr Haruta, Director of the Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology in Tsukuba, Japan, for his pioneering work on gold catalysis. Whilst at the Osaka National Research Institute (ONRI) in 1987, Dr Haruta discovered the very high catalytic activity of gold dispersed on oxide surfaces for the oxidation of carbon monoxide. Since then more than 40 papers have been published by his group on



Dr Haruta being congratulated on his award at the IPMI Conference by Dr David Thompson, Consultant to World Gold Council.

gold catalysis, focused on the high activity of gold nanoparticles. According to IPMI, what he has done is 'to demonstrate repeatedly and convincingly that gold, when properly used is an effective catalyst for new applications'. At present Dr Haruta's research activities include preparation, structural analyses, catalytic activity and sensing properties of gold nanoparticles deposited on metal oxides. ■

## Latest News – Reference Catalysts

We are pleased to report progress with the plans described in our previous issues. The first batches of two gold on oxide catalysts have been prepared at Süd Chemie, Japan and characterized at AIST, Osaka, and their catalytic activity evaluated. We hope to have samples available for supply shortly. Those researchers interested in obtaining a sample(s) should monitor the WGC website at [www.gold.org/value/sci\\_indu/gold\\_catalysts/refcat.html](http://www.gold.org/value/sci_indu/gold_catalysts/refcat.html), on a regular basis to keep up to date with latest developments. Once the catalysts are ready for supply, an order form will be available on the website.

A number of small samples of 10wt% gold on carbon catalysts has been prepared and evaluated at the University of Milan: their relevance to use in fuel cells is being investigated at Imperial College, London, by Dr Anthony Kucernak as part of a GROW project, so that the most appropriate sample can be chosen as a basis for the reference catalyst preparation. Further details will be published in our next issue. Readers comments are invited. ■

David Thompson  
[DTThompson@aol.com](mailto:DTThompson@aol.com)

## People:

Associate Professor Donka Andreeva



Associate Professor Donka Andreeva, Head of Laboratory for Design and Selection of Heterogeneous Catalysts, Bulgarian Academy of Sciences  
email: [andreev@ic.bas.bg](mailto:andreev@ic.bas.bg)

**Donka Andreeva has been studying heterogeneous catalytic reactions for the past 30 years, and since 1995 the focus has been on catalysis by gold for reactions such as the water gas shift and benzene oxidation.**

Identifying the relationships between preparation methods, gold dispersion, and the nature of the interactions between the gold, the support and the reactants have been the principal objectives of her research, as well as studying the mechanisms of the catalytic reactions. She is particularly interested in the use of gold catalysts in applications relevant to achieving increased environmental protection.

She is one of the Bulgarian research workers who played a leading role in creating the modern Bulgarian catalytic industry. She is co-author of 12 Bulgarian patents on new technologies for catalyst production for the manufacture of fertilizers and for petrochemical processes. She has been awarded a series of Bulgarian prizes for this activity as well as the Honorary Certificate of the World Organization for Intellectual Property Right Protection (1986) and two Golden Badges from the East-West Euro-Intellect Exhibition (1998).

Of the 60 papers published to date, Donka has 26 on catalytic gold, and has participated in a number of national and international meetings, including 'Catalytic Gold 2001', in Cape Town. As Associate Professor, Dr Donka Andreeva is the Head of the Laboratory for Design and Selection of Heterogeneous Catalysts at the Institute of Catalysis, Bulgarian Academy of Sciences.

Donka lives in Sofia - the capital city of Bulgaria, located in the foothills of the beautiful Vitosha mountains. She enjoys mountain walking, travelling and sightseeing, classical music, and growing flowers. ■

## GROW—

Funding for Applied Gold Catalysis Research, Development and Feasibility Studies

During 2002, 4 projects centred on applied gold catalysis research have been funded under the World Gold Council's GROW Programme. These include:

- An assessment of carbon supported gold as a catalyst for fuel cell relevant reactions
- Gold based DeNO<sub>x</sub> catalyst development for lean burn conditions
- Selective oxidation of CO in excess hydrogen
- Gold based catalysts for direct synthesis of hydrogen peroxide

Details of the GROW Programme can be found at [www.gold.org/value/sci\\_indu](http://www.gold.org/value/sci_indu)

## People on the move

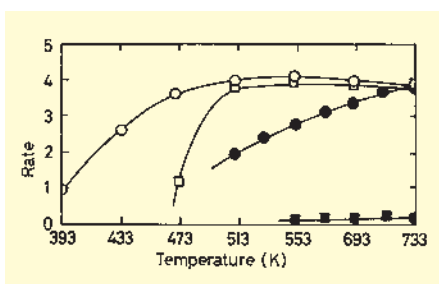
Professor Mike Cortie, formerly at Mintek, South Africa and working on the Project AuTEK, is now at the Institute for Nanoscale Technology, University of Technology, Sydney, PO Box 123, Broadway NSW 2007, AUSTRALIA. Professor Cortie is Chairman of the Gold 2003 Nanotechnology Committee.

# REACTION FOCUS : Gold-Catalysed Water Gas Shift

The new opportunities for gold catalysts in fuel cells were described in CatGold News Issue No 2. A key requirement for this is the supply of pure hydrogen to the fuel cell. The hydrogen is generally produced from an organic fuel such as methanol or natural gas, using a steam reformer, followed by the water gas shift (WGS) reaction, eg:



The results obtained by Dr Donka Andreeva's group at the Institute of Catalysis, Bulgarian Academy of Sciences, Sofia from the use of Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Au/Al<sub>2</sub>O<sub>3</sub> in the catalysis of the water gas shift are summarized in the Figure; the catalysts were prepared by coprecipitation and characterized using XRD and TEM. It is clear that the Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst is more active at lower temperatures than both the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> support and the CuO/ZnO catalyst currently



Temperature dependence of the catalytic activity of supported gold and base metal oxide catalysts in the Water Gas Shift. Starting reaction gas mixture was 4.88 vol% carbon monoxide in argon; water vapour partial pressure 223 Torr; SV 4000 h<sup>-1</sup>; 1 atm. Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (○); CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (□);  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (●); Au/Al<sub>2</sub>O<sub>3</sub> (■). Rates are expressed in mol m<sup>-2</sup> h<sup>-1</sup> x 10<sup>-2</sup>

used commercially; but Au/Al<sub>2</sub>O<sub>3</sub> prepared by coprecipitation has a very low activity. Preparation of Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> by deposition-precipitation produces more active catalysts than by coprecipitation.

Both Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> catalysts are active at low temperatures for the WGS. In the iron oxide-supported catalyst used for the work illustrated in the Figure, the gold particles had an average size of 3.5 nm and were situated in close proximity to the iron oxide crystallites.

At the 2001 conference on 'Catalytic Gold' in Cape Town, the activities of Au/CeO<sub>2</sub> catalysts for the WGS reaction were reported for the first time. The catalytic activity of the samples were evaluated for WGS activity over a wide temperature range (120 - 360°C). A 3wt% Au/CeO<sub>2</sub> sample had a high stability : after 3 weeks of operation, the final activity exceeds that obtained initially and this could be related to the high stability of the gold dispersion, with a tendency for the gold particles to decrease in size under the reaction conditions. The current status of gold catalysed water gas shift is summarized in a Gold Bulletin review (D. Andreeva, *Gold Bull.*, 2002, **35**(3)82; see also D. Andreeva et al, *Catal. Today*, 2002, **72**, 51).

Removal of the residual carbon monoxide from the hydrogen produced by WGS is another goal which could be met by using gold catalysts, and thus increase the efficiency of the fuel cell operation. ■

David Thompson

DTThompson@aol.com

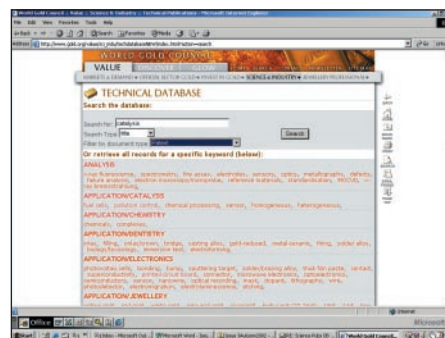
## References on Gold Catalysis via Internet

It is now possible to obtain a listing of the latest papers and patents on gold catalysis via the new Technical Database on the World Gold Council's website. Go to [www.gold.org/value/sci\\_indu/techdatabase](http://www.gold.org/value/sci_indu/techdatabase). Using the database will allow you to:

- Obtain a list of recent (or historical) publication references on a particular topic
- Keep up to date with which publications are carrying papers in your chosen field
- Identify the exact reference for a particular paper
- Search for other references by a particular author or on a particular subject

The database, compiled by FEM, Germany, is updated quarterly and you can either search just the latest update or the full database. Each entry has been characterised by **Keywords** You can either search:

- by these **Keywords** eg 'heterogeneous'
- by a word from the **Title**
- or by **Author Name**.



## Air Purification Prototype Unveiled

On the day that Harmony Gold Mining announced that it was joining the Project AuTEK initiative, aimed at pursuing research into new industrial uses for gold (See CatGold News Issue 1), the AuTEK team unveiled its first working prototype of a room temperature air purification unit that removes poisonous carbon monoxide from air. The unique feature of the unit is that it performs the operation at room temperature whereas other systems require an elevated temperature. Contact: Dr Elma van der Lingen, Mintek, [elmavdl@mintek.co.za](mailto:elmavdl@mintek.co.za)

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progresses. In addition to this training in management and leadership they will be given an industrial perspective of project management and R&D, including experience of scale-up and high throughput screening and combinatorial methods, during the 4 weeks that they will each spend in industry. Each post-doc will spend a total of 2-3 months in the laboratories of participants other than their host department in order to learn specialised techniques and gain the aforementioned industrial experience.

The participating organisations and team leaders in the AURICAT Network are as follows:

**GJ Hutchings**, The University of Wales Cardiff, UK; **AO Taylor**, The University of

Salford, UK; **D Lennon**, The University of Glasgow, UK; **HJ Freund**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany; **ASK Hashmi**, Universität Stuttgart, Germany; **M Rossi**, Università' Degli Studi Di Milano, Italy; **A Corma**, Universidad Politecnica De Valencia, Spain; **JA Moulijn**, Technische Universiteit Delft, The Netherlands; **H Lansink-Rotgerink**, Degussa AG 10, Germany; **BA Murrer**, Johnson Matthey Technology Centre, UK; **RP Tooze**, Syntex, ICI Chemicals & Polymers Ltd, UK; **G. Vecchiato**, Süd Chemie MT Srl Italy and **DT Thompson**, World Gold Council, UK. ■

*I. GC Bond & DT Thompson, Cat Rev-Sci Eng, 1999, 41, 319-388*