

# The 18th Meeting of the North American Catalysis Society, Cancun, Mexico, 1 – 6 June 2003

This conference proved to be an important event, with many stimulating talks on the applications for catalyst technology in pollution control, chemical processing and fuel cells. A significant new profile emerged for gold catalysis with a realization of its potential for new applications, many of which may take advantage of its unique low temperature performance characteristics. There were 14 oral and 7 poster presentations where the principal theme was catalysis by gold (including one from WGC which was well received and stimulated much discussion); and there is an increasing realization that gold is an exciting new topic. In addition the current issue of the journal CATTECH containing an article by Graham Hutchings and Mike Scurrall on 'Designing Oxidation Catalysts' contains a significant case study on gold catalysis, and this was distributed to all 600 delegates.

Presentations where catalysis by gold was discussed included the following:

## Catalysts for Air Pollution Abatement

- 1 **Potential of Catalysis by Gold for Fuel Cell and Pollution Control Applications**, by Christopher W. Corti, Richard J. Holliday and David T. Thompson, *World Gold Council, London, UK*

## Catalysis of the Water Gas Shift

- 2 **Deactivation and Regeneration of Nanocrystalline Gold Water Gas Shift Catalysts**, by Chang Hwan Kim, Shyamal K. Bej and Levi T. Thompson, *University of Michigan, Ann Arbor, USA*
- 3 **Water Gas Shift Activity of Low-Content Gold/Cerium Oxide Catalysts**, by Qi Fu, Howard Saltzburg and Maria Flytzani-Stephanopoulos, *Tufts University, Medford, MA, USA*

## Catalysis of Organic Reactions

- 4 **Molecularly Promoted Noble Metal Catalysts for Chemo- and Enantioselective Gas Phase Hydrogenation**, by Matthias von Arx, Johnathan Bartley and Graham J. Hutchings, *Cardiff, UK*
- 5 **Heterogeneous Gold Catalysts: A Versatile Tool for the Synthesis of Fine Chemicals**, by Candida Milone, Roberta Ingoglia, Maria Letizia Tropeano, Giovanni Neri, Carmelo Crisafulli and Signorino Galvagno, *Universities of Messina and Catania, Italy*
- 6 **Propylene Epoxidation over Au/TS-1**, by Nora Yap, David H. Wells, Jr., Bradley Taylor, Kendall T. Thomson, Jochen A. Lauterbach and W. Nicholas Delgass, *Purdue University, IN and University of Delaware, USA*
- 7 **Glucose Oxidation over Supported Gold Catalysts**, by Peter Claus, Sabine Schimpf, and Yücel Oenal, *Darmstadt University of Technology, Germany*
- 8 **Synergistic Effect of Gold in Au/Pd Catalysts during HDS Reactions of Dibenzothiophene**, by Anna Maria Venezia, Valeria La Parola, Giulio Daganella, Barbara Powalec and Jose Luis Garcia Ferro, *ISMN, Palermo, Italy and CSIC, Catblanco, Madrid, Spain*

## Fundamentals in Studies in Metals and Oxides

- 9 **Potential Role of Hydroxyl in CO Oxidation over Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>**, by C.K. Costello, J.H. Yang, Y. Wang, L.D. Marks, M.C. Kung and H. Kung, *Northwestern University, Evanston, IL, USA*

## Catalysis by Metallic Nanoparticles

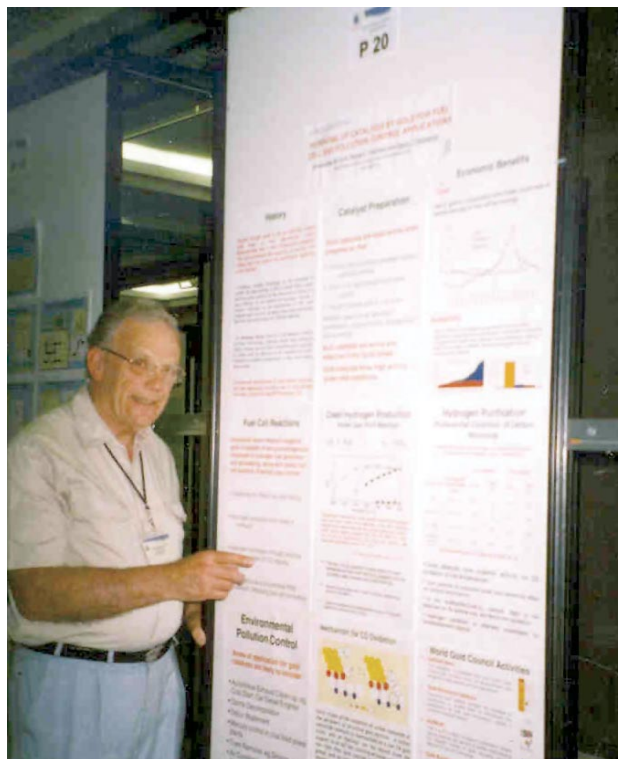
- 10 **Dendrimer Templates for Compositional Control of Bimetallic Catalysts** by Huifang Lang, R. Alan May, Brianna L. Iversen, Bert D. Chandler, D. Sam Deutsch, Lorna Sotto and Michael D. Amiridis, *Trinity University, San Antonio, Texas and University of South Carolina, Columbia, USA*
- 11 **High Surface Area Model Catalysts: Platinum and Gold Uniform Nanoparticles Encapsulated in Mesoporous Silicate Materials**, by Robert M. Rioux, Zolton Konya, Victor F. Puntes and Gabor A. Somorjai, *University of California and Lawrence Berkely National Laboratory, Berkeley, USA*
- 12 **Activation of Gold Nanoparticles on Titania: Adsorption and Reaction of SO<sub>2</sub> on Au/TiO<sub>2</sub>**, by Gang Lui, Jose A. Rodriguez, Tomas Jirsak, Jan Hrbek, Zhipeng Chang, Joseph Dvorak and Amitesh Maiti, *Brookhaven National Laboratory, Upton, NY and Accelrys Inc, San Diego, CA, USA*
- 13 **Interactions of H<sub>2</sub>, D<sub>2</sub> and Acrolein with Surfaces of Supported Silver- and Gold Catalysts**, by Michael Bron, Peter Claus, Jens Hohmeier and Ecgenii Kondratkenko, *Darmstadt University of Technology and Institute for Applied Chemistry Berlin, Germany*

- 14 **CO Oxidation Catalysed by Supported Gold: Influence of Oxidation States of Gold on Catalytic Activity**, Javier Guzman and Bruce C. Gates, *University of California, Davis, USA*
- 15 **Aerosol Synthesis of Thermally Stable Mesoporous Catalysts**, by Mangesh Bore, Hien N. Pham and Abhaya K. Datye, *University of New Mexico, Albuquerque, USA*

#### Nanocatalysts

- 16 **Characterization and Reactivity of Gold Nanoparticles Supported on TiO<sub>2</sub> Prepared by Deposition Precipitation with Sodium Hydroxide and Urea**, Rodolpho Zanella, Catherine Louis, Suzanne Giorgio, Claude R. Henry and Chae-Ho Shin, *CNRS Université Pierre et Marie Curie, Paris, France*
- 17 **Novel Method of Preparation of Gold Nanoparticles by Ion Exchange**, by I Tuzovskaya, N. Bogdanchikova, V. Gurin, A. Datye, A. Pestryakov and A. Simakov, *Tomsk Polytechnic University, Russia, UNAM, Ensenada, Mexico, BSU, Minsk, Belarus and University of Mexico, Albuquerque, NM, USA*
- 18 **Controlled Preparation of Gold Nanoparticle Catalysts in Porous Materials; Synergistic Interplay of Self-Assembly, Nucleation and Topology**, by Sheng Dai, Byungwan Lee, Hoanguo Zhu, Zongtao Zhang and Steven H. Overbury, *Oak Ridge National Laboratory, TN, USA*
- 19 **EXAFS Characterization of Gold Nanocatalysts**, by Viviane Schwartz, David R. Mullins, Hoanguo Zhu, Byungwan Lee, Sheng Dai and Steven H. Overbury, *University of Delaware, Newark, USA and Oak Ridge National Laboratory, TN, USA*
- 20 **Synthesis, Structural Characterization and Catalytic Performance of Gold-Nanoparticle Catalysts on Mesoporous Supports**, Steven H. Overbury and Sheng Dai, *Oak Ridge National Laboratory, TN, USA*
- 21 **Synthesis and Structural Characterization of Model Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts**, by Juan C. Fierro, Javier Guzman and Bruce C. Gates, *University of California, Davis, USA*

A broader range of useful methods for the preparation of gold catalysts is now emerging and, for example a two step impregnation procedure developed by Datye et al (University of New Mexico, USA) gives activities comparable with catalysts prepared by deposition precipitation. There is clear evidence that the presence of halide inhibits the activity of gold catalysts and non-halide routes are therefore under investigation (e.g. by Bruce Gates et al, University of California, Davis). Both the nanoparticulate and metal-support interaction aspects seem to play a part in activating the gold on the support surface and the relative importance



of these and pre-treatment factors such as optimal calcination temperature and choice of gases are under investigation. The above list includes papers relevant to both large scale and fine chemicals production as well as pollution control and fuel cell applications.

Significant new results included the report by José Rodriguez et al (Brookhaven National Laboratory, USA) that Au/TiO<sub>2</sub> is 5 - 10 times more active than pure TiO<sub>2</sub> for the Claus reaction ( $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 3\text{S}_{\text{solid}}$ ) and for the reduction of SO<sub>2</sub> by CO, and these results could have significant relevance to development of new catalysts for pollution control.

Now that gold has been established as a catalyst in its own right the addition of other metals is being used to increase the activity and selectivity of gold catalysts. The advantageous use of Au/Pd catalysts in commercial processes for the manufacture of vinyl acetate is now well established. Anna Maria Venezia et al (Palermo, Italy and Madrid, Spain) have found that in the hydrodesulfurization of dibenzothiophene conversion increases by a factor of >6 for 1:1 Au/Pd on silica compared with Pd/SiO<sub>2</sub>, and that Au/SiO<sub>2</sub> is more active than Pd/SiO<sub>2</sub>, although the gold catalyst is less active than the alloy catalyst. A dendrimer template approach is being investigated for the compositional control of Au/Pt catalyst preparation by Bert Chandler et al (San Antonio, Texas).

Ways of increasing the durability of gold catalysts is a topic which needs more study but there are encouraging signs that the activity can be preserved even at several hundred

degrees. There is also clear evidence that deactivated catalysts can be regenerated for CO oxidation and Water Gas Shift activity.

Harold and Mayfair Kung's group (Northwestern University, USA) has done some very interesting mechanistic work with gold on alumina catalysts for CO oxidation. Water and hydrogen treatment have been used to revive deactivated catalysts. The role of water is particularly intriguing. The fact that very small amounts of chloride deactivate the catalyst implies that the intrinsic activity of gold is probably higher than has yet been recorded: more experiments with non-halide preparative routes are called for! The relative importance of and inter-relationships between metallic and oxidized gold in the mechanism was discussed by several speakers.

The activity of supported gold at ambient temperatures and below remains a unique feature of catalysis by gold. The fact that gold is much more plentiful than the platinum

group metals and its price is more stable and lower than that of platinum also augers well for the future of applications for gold catalysts (1).

The present author was invited by Professor Gabor Somorjai (UC Berkeley) to act as editor for a special edition of 'Topics in Catalysis' on 'Catalysis by Gold' to be published in 2004.

For the first time in a major multi-faceted international catalysis conference, it was apparent that catalysis by gold has become respectable amongst catalysis practitioners and many of them are optimistic about the likely number of new applications.

David Thompson

## Reference

- 1 C.W. Corti, R.J. Holliday and D.T. Thompson, *Gold Bull.*, 2002, **35**, 111

# Nanoparticle Assemblies: RSC Faraday Discussion 125, Liverpool, UK, 14 – 16 July 2003

**This was a stimulating meeting attended by 120 delegates, from 16 different countries overseas. Of the 65 presentations and posters, about half included work on gold. The chairman of the organising committee, Professor David Schiffrin's innovative pioneering paper (1), led to gold being firmly established as a key element in the field of nanotechnology. This was the first to demonstrate the formation of monolayer-protected clusters when thiols react with small gold particles (2). Since these nanoparticles protected by thiol-containing ligands are easy to prepare and stable, gold is now key to this new fast-developing research area.**

Professor Uzi Landman (Georgia Institute of Technology, USA) presented an introductory lecture entitled 'Small is Different: Self-Selection, Assembly and Organisation at the Nanoscale'. The nanoscale regime produces novel phenomena: these are not merely a scaling down from the

macroscale regime – above the nanoscale, properties are predictable, but with nanotechnology a non-scaleable, non-predictable regime occurs, resulting in novel phenomena. In this regime interactions caused by hydrogen bonding, dipolar and Van der Waals forces, hydrobobic/hydrophilic interactions, surface tension, capillarity, physisorption and chemisorption, and gravity etc become important. Considerations include self assembly, self selection, abundance, size (magic numbers), shape, structure fluxionality, and spontaneous symmetry bonding and breaking, and there is a hierarchy of effective forces. Research in the area of metal nanoparticles is driven by the unusual optical, electronic and chemical (eg catalytic) properties of the materials which can be constructed from them.

As for all Faraday Discussions, the rest of the speakers were given five minutes to introduce their paper, which was then open for substantial discussion. Some of the gold papers presented included:

'*Gold Nanoparticle/Organic Linker Films: Self Assembly, Electronic and Structural Characterization, Composition and Vapour Sensitivity*' by Tobias Vossmeier et al, Sony International (Europe) GmbH, Stuttgart, Germany

'*Electrochemical and Optical Properties of Two Dimensional Electrostatic Assembly of Gold Nanocrystals*' by David Fermin et al, Ecole Polytechnique Fédérale de Lausanne, Switzerland

'*Hyper-Rayleigh Scattering of Gold Nanorods and Their Relationship with Linear Assemblies of Gold Nanospheres*' by P.-F. Brevet et al, Université Claude Bernard Lyon 1, France

'*Au/Ag Bimetallic Nanoparticles: Formation, Silica-Coating and Selective Etching*' by Luis M. Liz-Marzan, Universidade de Vigo, Spain

'Wiring Redox Molecules with Nanoparticles' by Richard Nichols, David Schiffrin et al, University of Liverpool, UK

'Adaptive Chemistry of Bifunctional Gold Nanoparticles at the Air/Water Interface. A Synchrotron X-Ray Study of Giant Amphiphiles' by Thomas Bjornholm, University of Copenhagen, Denmark.

'Growth, Conductivity, and Vapour Response Properties of Metal Ion-Carboxylate Linked Nanoparticle Films' by Royce W. Murray et al, University of North Carolina, Chapel Hill, USA.

In this last paper the change of electronic conductivity could be exploited for the sensing of organic vapours.

A very effective poster session was held and lively discussions continued for at least three hours. Amongst the presentations were two from Sony International (Europe) entitled 'Molecular Tuning of Conductivity in Molecule Nanoparticle Composites from Insulating to Metallic Behaviour', by H.-G. Nothofer et al and 'Self-Assembled Gold Nanoparticle/Alkanedithiol Films: Preparation, Electron Microscopy, XPS-Analysis, Charge Transport, and Vapour Sensitivity' by Y Joseph et al, and another entitled 'Gold Nanoparticles as Templates for the Realization of Functional Molecular Assemblies' by Lucia Pasquato et al from the University of Trieste, Italy. An interesting presentation was given by Wembo Song of Hokkaido University, Sapporo, Japan entitled 'Preparation and Electrochemical Properties of Nanoarchitectures of Gold Nanoclusters Protected by Mixed SAMs and Ionic Polymers'. A poster relevant to the interface between gold nanotechnology and biology was entitled 'Enzymic Manipulation of DNA/Gold Nanostructures' by A.G. Kanaras, Matthias Brust et al of the University of Liverpool, UK. The importance of gold nanotechnology in the field of

catalysis was represented by a paper entitled 'AuPd Bimetallic Nanoparticles: Synthesis, Electronic and Structural Characterization, Reactivity', by Maria Casaletto et al of the University of Palermo, Italy.

Most of the technology is still in the early stages, but applications can be foreseen in sensors for a variety of substrates in both gases and liquids. Monitoring body fluids for selected substances by developing colour changes has already been demonstrated, and many of these effects operate at room temperature. New ways of depositing electronic circuitry can also be foreseen, and new applications in materials and decorative technology are emerging (2). Catalysis by nanoparticulate gold is already an important part of the gold nanotechnology scenario, with applications being developed in chemical processing, pollution control and sensing. Use of nanoshells, nanorods, clusters and layers of gold will lead to the identification of further exploitable properties.

Those responsible for organizing this meeting will be encouraged by the free flow of ideas and stimulating discussions that resulted. It was evident that a wide range of applications for gold nanotechnology could emerge as the innovative research in this area continues.

David Thompson

## References

- 1 M. Brust, M. Walker, D. Bethell, D.J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801
- 2 C.W. Corti, R.J. Holliday and D.T. Thompson, *Gold Bull.*, 2002, **35**, 111

## ATTENDING A TECHNICAL CONFERENCE INVOLVING GOLD?

In keeping with its objective of publishing the latest progress, an aim of *Gold Bulletin* is to publish reports of relevant conferences that involve the science, technology and applications of gold.

The Technical Editor would like to hear from readers planning to attend such conferences and who are willing to write a conference report for publication. A small honorarium is payable for reports published.

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