

# Conference Highlights

## 10th International Symposium on Catalyst Deactivation, Harnack Haus Berlin 5-8 February 2006

This was the tenth in a series of 'traditional' conferences on catalyst deactivation, and was organized by Dechema. It was broad ranging including new areas of catalysis (eg gold), traditional processes (eg Fischer Tropsch, methanol synthesis) and homogeneous catalysis. There was good representation from both academia and industry: the scene was aptly described by one delegate in that academics emphasize investigations on what makes catalysts active whilst industrialists apply their minds to solving durability aspects. When homogeneous catalysis works well in an industrial sense, it works really well, under mild conditions, and deactivation is usually not a problem. Since gold has the advantage of working under mild conditions it could eventually have advantages of the same kind as homogeneous, once the durability / stability problems are solved, in both homogeneous and heterogeneous applications.

Of the 34 oral presentations, 3 were principally on catalysis by gold and of the 50 posters 2 were on gold catalysis, and the advantages of adding gold to a nickel steam reforming catalyst was emphasized by a Haldor Topsoe speaker (P L Hansen). Hajo Freund described results which clearly indicate that gold is unique, so solutions to gold deactivation challenges may also be unique!

### Highlights of Gold Presentations

#### Talks

##### 1 Prof Jacob Moulijn, Delft Technical University, The Netherlands

This talk, entitled 'Catalyst Deactivation and Process Design' was exemplified by the Delft work on propene epoxidation using gold catalysts (part of the AURICAT project). The principal points were that:

- 1 Choice of support is important and  $\text{TiO}_2/\text{SiO}_2$  is better than  $\text{TiO}_2$
- 2 Calcination procedures affect performance
- 3 Au sintering is accompanied by change in oxidation state of the gold
- 4 Poisoning of the catalysts probably involves carbonate/formate formation.

In a WGS reactor regime ICI Cu/Zn catalyst was more effective than  $\text{Au}/\text{Fe}_2\text{O}_3$  but these gold results were not optimised. The work of Graham Hutchings' group (Cardiff, UK) on hydrogen peroxide synthesis using Au-Pd catalysts highlighted the fact

that chloride is not an inhibitor in liquid phase catalysis using gold. The increased activity of Au-Pd compared with either Au or Pd on its own was emphasized.

##### 2 Prof Hajo Freund, Fritz Haber Institute, Berlin

Quite a large proportion of this talk, entitled '*Nanoparticles on Oxides as Models for Heterogeneous Catalysts: An Atomic View*', was on surface science related to gold catalysis. Au-CO bonds formed at 8 K show an IR stretching frequency representing a position on a terrace site which is special effect of gold. Above 30 K the bonding is on edge sites and not special. Overall behaviour shows that Au is unique and Professor Freund agreed that this uniqueness arises from the relativistic effect of gold which is at a maximum.

##### 3 Prof Harold Kung, Northwestern University, USA

This lecture was solely on the gold catalysis work carried out recently by Kung's group. The talk was entitled '*Understanding Catalytic Active Sites by Activation and Deactivation Studies*'. The generation (activation) and suppression (deactivation) of activity are sensitive indicators of the availability of active sites. From studies on the use of  $\text{Au}/\text{Al}_2\text{O}_3$  and  $\text{Au}/\text{TiO}_2$  for CO oxidation it was concluded that metallic Au is necessary for activity although the presence of a little oxidized gold might also be necessary. The presence of halide deactivates the catalyst but the presence of water promotes activity, probably by creation of OH ions on the catalyst surface. Water can also be used to re-activate catalyst deactivated by deposition of carbonate. With  $\text{Au}/\text{Al}_2\text{O}_3$  the rate of CO oxidation at room temperature declines rather rapidly but addition of water to the CO feed stream gives a steady reaction rate.

#### Posters

1 *Coprecipitated Au-Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalysts for methane emissions abatement: influence of support composition on catalytic performance and deactivation*, by Leonarda F. Liotta, G. Di Carlo, A. Longo, G. Pantaleo, Anna-Maria Venezia and G. Daganello, Palermo, Italy.

$\text{Au}/\text{Co}_3\text{O}_4$  is very active for methane oxidation but the activity decreases rather rapidly. Addition of  $\text{CeO}_2$  to the support stabilizes the catalyst for at least 65 h at 600°C. A low concentration of methane was used (0.3 vol%). It was claimed that catalysts would be best for alleviating engine cold start problems.

2 *Deactivation of Au/CeO<sub>2</sub> catalysts in water-gas shift reaction from idealized to realistic conditions*, A. Karpenko, V. Plzak, B. Schumacher and R.J. Behm, Universität Ulm.

$\text{Au}/\text{CeO}_2$  catalysts are highly active for the WGS reaction and have been investigated for CO removal from hydrogen streams used to feed PEM fuel cells. Rates of deactivation were evaluated during WGS. Four different deactivation mechanisms are possible: (i) gold particle sintering, (ii) sintering of ceria, (iii) reduction of ceria in excess of the ideal ratio of  $\text{Ce}^{3+}/\text{Ce}^{4+}$  surface species, and (iv) carbonate/

hydrocarbonate blocking of active sites. Some growth of Au particles to above 3 nm was observed but the main cause of deactivation was the adsorbed carbonate species produced.

David Thompson  
DTThompson@aol.com

## **TMS2006 Conference and Exhibition San Antonio, Texas, 12-16 March 2006**

This is one of the largest materials engineering focused conferences in the world. World Gold Council had a small stand at the trade show, allowing it to publicise its programmes supporting the industrial uses of gold including *Gold Bulletin*, the business directory UtiliseGold ([www.utilisegold.com](http://www.utilisegold.com)) and the GOLD 2006 conference ([www.gold2006.org](http://www.gold2006.org)).

Although the light metals (Al and Mg) were the predominant theme of the event (for which there were approximately 4000 attendees), there was a good spread of other material technologies including the precious metals. There were about a dozen papers concerning gold, including:

*Deformation Behaviour of Nanoporous Gold* was presented by Erica Lilleodden from the Forschungszentrum, Karlsruhe. She presented a study on the deformation behaviour of nanoporous gold. Their material was made by electrochemical dissolution of AuAg sheets with a nominal grain size of 100  $\mu\text{m}$  and this results in a structure with pore and wall size of the order of 20 nm. The presentation looked at mechanisms of deformation in this fine-structured, coarse-grained material as well as microstructural characterization. It was not clear what, if any, end application they had in mind.

*Deposition of Conductive Films on Electronic Substrates by Using Gold Nanopowders* was presented by a team from National Cheng Kung University and National Dong Hwa University. The rationale for this work was the fabrication of micro-interconnects without using the conventional lithography-etching process. In this study, gold particles with an average size of 5nm were selected. Utilizing spin coating and ink-jet printing, they were deposited onto commonly used electronic substrates, Cu, Ni and Al. After a curing treatment, the degree of continuity and adhesion strength of the coated film on the Ni substrate was better than that on the Cu substrate, which was in turn better than the Al substrate. Electrical resistivity of the gold film produced and the interfacial reactions between the films and the substrates were also examined. They compared well with the performance of commercial gold nanoinks sold by ULVAC.

*Effect of Copper Solution on Deformation Behaviour of Nanocrystalline Gold*, by a team from Lawrence Livermore National Laboratory, focused on an interesting aspect of nanocrystalline gold with copper solution additions in the range of 0-12 wt.% and grain sizes below  $\sim 10$  nm. Samples

were prepared using an electrodeposition technique. These nanocrystalline foils have a typical thickness of above 10  $\mu\text{m}$ , and thus allowed the researchers to carry out mechanical property assessment using traditional mechanical characterization techniques, such as tensile tests and instrumented nanoindentation experiments. The Young's modulus, hardness, tensile strength, and tensile ductility were determined as a function of grain size and solid solute content. Special attention was also paid to interpret the copper solid solute effect on strain rate sensitivity of these materials. The evidence suggests that alloying could not only substantially improve the mechanical properties of nanocrystalline materials including gold, but also fundamentally alter their deformation behaviour.

*Photo-Synthesis of Nano Gold Particles for Drug Delivery* by a group led by Prof. Yang from the University of Taipei, reported a simple approach to generate gold colloidal from  $\text{HAuCl}_4$  aqueous solution by synchrotron x-ray irradiation at room temperature, without a reducing agent. It was also observed that the addition of  $\text{NaHCO}_3$  easily modified the size and size distribution of gold nanoparticles. Under optimal conditions, the precipitated nanoparticles were well dispersed and with uniform size,  $\sim 10$  nm. They state that the Au nanoparticle solution prepared with this simple, clean and very fast process without toxic reductant is biocompatible – and could be used for surface modification and drug attachment procedures in the same bath. Their preliminary drug carrying experiment showed that the produced gold nanoparticles could successfully carry anti-tumour drug and possess potential for drug delivery applications. Further studies on accessing the capacity of drug loading, delivery and release characteristics are currently underway.

*Thickness Effects on the Plasticity of Gold Films* was presented by Megan J. Cordill from the University of Minnesota with colleagues from Sandia National Laboratories, Washington State University and the University of South Florida. Gold films are used in advanced applications where limited film thickness can affect the film's mechanical properties. It has been shown that as film thickness decreases the energy required for film delamination also decreases. This decrease is most likely due to the amount of plasticity available for deformation. To examine these effects, nanoindentation was employed to simulate a sharp crack on the film's surface. The indenter tip causes deformation by dislocation nucleation. The time dependent elastic recovery of the indents was monitored using scanning probe microscopy techniques. Gold films (40 nm and 200 nm) were indented using three tips: a blunt berkovich, a sharp berkovich, and an ultra sharp cube corner. Each tip demonstrated different behaviour as a function of film thickness and initial indentation depth.

*Overview of the Use of Direct Write Technologies for Use in Sensor Developments and Fabrication*: was presented by James W. Sears from South Dakota School of Mines and Technology. Direct Write Technologies (DWT) provide a tool for the novel manufacturing of various sensors and are also

being used in electronics, engineered structures, and tissue engineering. James described the precursor materials used as inks and pastes for the Direct Write Technologies, which are comprised of nano-scale particles (i.e., Ag, Au, Pt). The presentation gave an overview of these technologies. With reference to gold (following questioning) he claimed that they had had significant difficulties with 'balling' of gold and that one needed more complicated surface groups on the gold to control this.



*San Antonio, Texas – the location for TMS2006.*

Richard Holliday  
Manager, Industrial Sector  
World Gold Council