CatGold NEWS

ISSUE No. 16

SUMMER 2008

A newsletter on developments and progress in gold catalysis and its applications

New support for Gold Catalysis Research

Grant from Dow to respond to Methane Challenge

Two academic groups led by Cardiff University, UK and Northwestern University USA have been awarded grants by Dow Chemical totalling $6.4 million over 3 years to devise ways of converting methane into industrially important olefins and olefin precursors (M Reisch, *Chem Eng News*, January 28 2008, p 14).

Prof Graham Hutchings will lead the Cardiff team in collaboration with experts in microscopy at Lehigh University, USA and chemical engineering at Imperial College, London, UK. Hutchings rates the direct oxidation of methane as the most important remaining challenge in catalysis and he thinks that nanoparticle gold catalysts could provide an answer.

The main component of natural gas is methane and there are large reserves of this in many parts of the world. The conversion of methane into ethene, propene, or their precursors by any means other than costly syn gas chemistry has proved to be elusive, but Dow's global business director, Mauro Gregorio is seeking alternative feedstocks which could act as a new starting point for chemicals and plastics currently made from costly naphtha and natural gas liquids used today.

The Northwestern team will be lead by Prof Tobin Marks and will try and capitalize on recent alkane oxidation successes, and use less aggressive and more selective oxidants to provide olefins or other useful feedstocks.

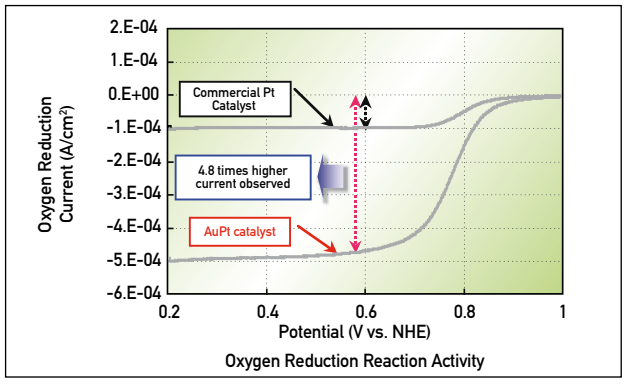
WORLD GOLD COUNCIL

Hitachi Maxell announce Au-Pt Catalyst for PEMs

Hitachi Maxell has developed a new catalyst for use in the oxygen reduction reaction at the cathode of a polymer electrolyte fuel cell (PEFC). The inclusion of gold in the catalyst reduces the cost and achieves ca 4.8 times higher oxygen reduction current per unit area than is given by Pt alone.

The new Au-Pt catalyst on activated carbon is prepared using nanoparticle synthesis technology based on citrate reduction, developed in-house. The two metals are not fully alloyed because the Au-Pt phase diagram has a large miscibility gap but the catalyst is acid resistant. The Au-Pt catalyst is 2-3 nm in size and is prepared using citric acid as reducing agent at 373 K.

This significant advance is foreseen as assisting the development of fuel cells for applications requiring a large current such as power sources for automobiles and homes. Maxell are continuing R&D on the nanotechnology with a view to practical application in polymer electrolyte and direct methanol fuel cells.



The Oxygen Reduction Reaction Activity of Gold-Platinum (AuPt) and Commercial Platinum (Pt) Catalysts Deposited on the Same Conductive Carbon Support (Specific Surface Area: 800 m²/g)
The oxygen reduction currents were normalized by unit surface area of the catalysts. Oxygen reduction currents 4.8 and 3.2 times higher than those of commercial platinum catalyst at 0.6 V and at 0.8 V versus normalized hydrogen electrode (NHE), respectively, were observed

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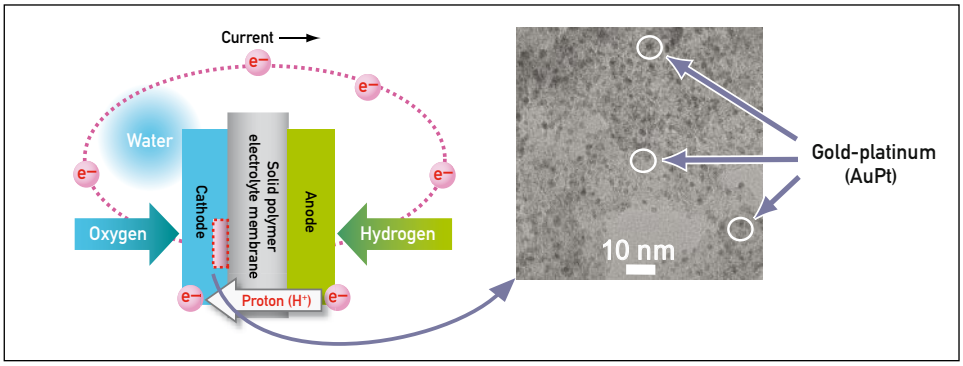
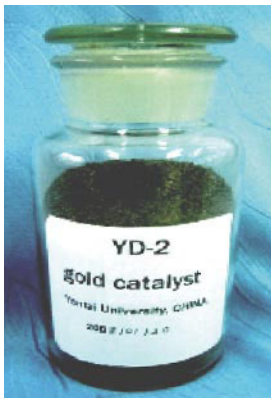


Electron Microscope Photograph of Gold-Platinum (AuPt) Catalyst Deposited on a Conductive Carbon Support
The dark grey or black areas are the gold-platinum catalysts, and the light grey areas are the carbon support. The gold-platinum catalyst particles are 2 to 3 nanometer in size.

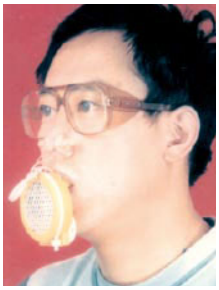
See http://www.maxell.co.jp/e/release/20080327.html for more information ■



A Stable Supported Nanogold Catalyst

On the basis of 16 years' R&D experience, the Institute of Applied Catalysis in Yantai University, Shandong, China has developed a novel stable gold catalyst (YD-2) with a gold loading of about 1.1wt% on a ferrite-modified alumina support. This catalyst has been evaluated for use in a standard filtering respiratory protective device by three Chinese Organizations, i.e. Changsha Mine Safety Equipment Supervision Center, Shanxi Xinhua Chemical Corporation Limited and Foshan Nahai Jinling Safe Guarding Equipment Factory under conditions at inlet gas concentrations of 0.25-1.5 vol % CO, 30/85/95L/min, 92-96% RH and ambient temperature. The residual concentration of CO is <100ppm and the inhalation temperature is ≤40°C. An example of the results achieved in the Foshan Factory is given in Figure 1. The test results are comfortably within the demanding standard of the European EN403 code criteria (200 ppm breakthrough after 15 minutes) and China GA209-1999 (equivalent to EN403:1993). 16-20 grams of YD-2 gold catalysts are sufficient for the use in a CO filter for a mini-type self-rescuer (only 120g total weight, see photo opposite), which can work continually for 8-10 hours and is designed without a dryer or cooling unit. The combination of YD-2 catalyst with other catalysts (active carbon, HCN removal catalysts, etc) can be used in masks which also provide protection from other toxic gases, such as HCl and HCN.

The catalytic activity of YD-2 doesn't change when stored in a sealed container for 4 years (experiments still continuing) and 95% of activity was obtained after the catalyst had been exposed to air for about 2 months. In another application, YD-2 catalysts are placed in a sealed CO_2 laser to promote the combination of CO with O_2 to give CO_2, so it is not necessary to supply CO_2 within 1 year for a working CO_2 laser. A set of patents has been filed on the composition and preparation of YD-2 catalyst and its potential applications in the fertilizer industry and safety projects. Currently, the gold catalyst group in the Institute is studying long-term catalyst stability on exposure in air in order to further expand the applications of gold catalysts.



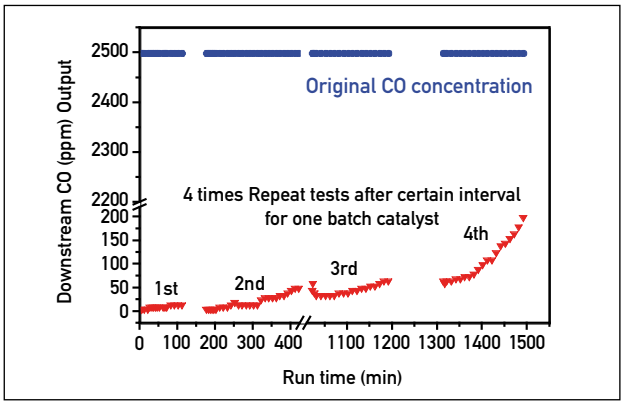
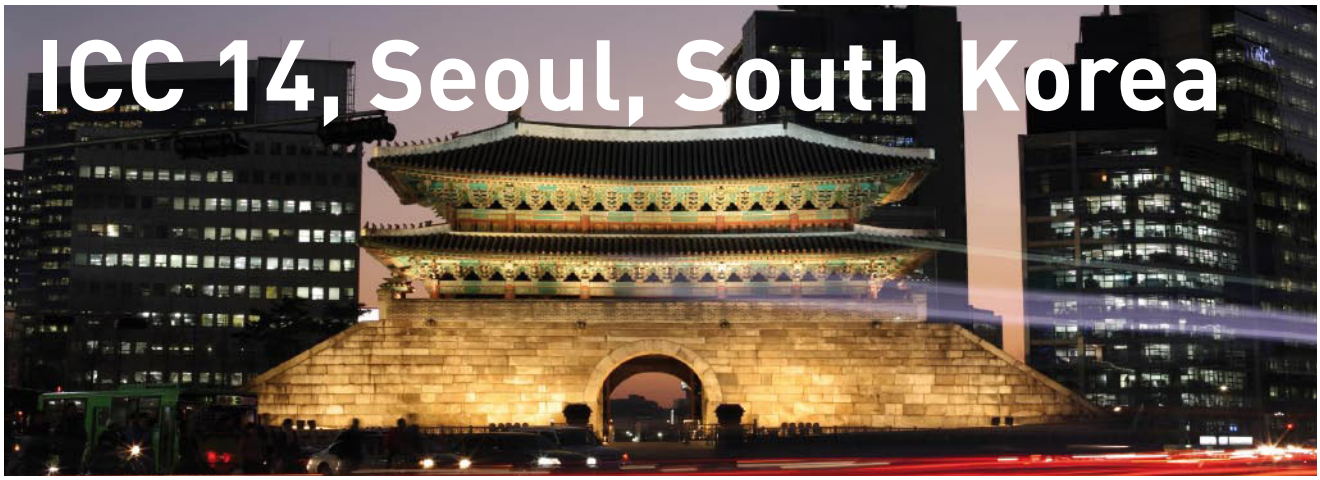


Figure 1
CO test on a standard filtering respiratory protective device [Approx. 2500ppm CO in air, RH: 92±2%; 25±1°C, GHSV: 43373h-1; YD-2 catalysts (0.8-1.5mm in diameter): 22g; bed: 65mm diameter; pressure drop (breathing resistance determined at 95L/min): 420Pa]

For more information, please contact Professor Lidun An via aci@ytu.edu.cn or Professor Caixia Qi via qicx1@yahoo.com ■



ICC 14, Seoul, South Korea

13-18 July 2008

The 14th International Congress on Catalysis will be held in Seoul, South Korea 13-18 July 2008 (http://www.icc2008korea.com/), and its themes include 'Innovations in catalyst design', 'New findings in reaction mechanisms', 'Advances in catalytic reaction engineering', 'Catalysis in energy / fuel production'. 'Catalysis for fine chemicals/ industrial chemicals production', and 'Sustainable green catalysis'. World Gold Council and Project AuTEK will be making a presentation entitled 'New commercial opportunities for gold catalysts' in the special industrial technology session.

WGC will have an exhibition stand in collaboration with the South Africa organisation Mintek who are seeking to promote their AURO*lite*™ range of gold catalysts produced in conjunction with gold mining company Anglogold-Ashanti under the Project AuTEK initiative. In addition to AuTEK, exhibitors at the WGC exhibition stand will include Nanostellar (California, USA), Novax (Taiwan), and Yantai University (China) who have diesel oxidation catalysts and protective gas masks containing gold catalyst to display.

There is also a pre-conference in Kyoto, 8-12 July on 'Creation and Control of Advanced Selective Catalysis' (http://www.shokubai.org/intern/ICC-Pre/) where there will be a significant number of presentations on gold catalysis and its applications ■

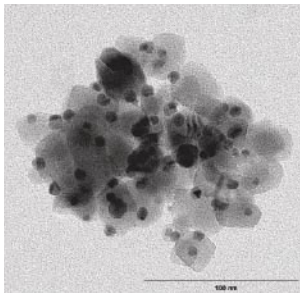
Signi cant increase in Gold Catalyst production by Project AuTEK

Project AuTEK, South Africa, reports that it has seen a drastic increase in demand for its gold catalysts since the start of 2008.

In 2007 AuTEK distributed some 20kg of gold catalyst in total, and has already sold 100kg to date in 2008, with this material generating further interest from end-users especially in the field of CO oxidation. AuTEK also sees this significant progress as a payoff to its marketing efforts in collaboration with the World Gold Council. With this increase in demand AuTEK can now justify the further scale-up of its production process from the present 15 kg level to 65 kg batches. End-users wishing to purchase material are encouraged to contact catalysts@autek.org, AuTEK produces powdered or shape formed gold catalysts based on TiO_2, Al_2O_3 and ZnO supports.

For further information please see www.autek.org ■

Auro*lite*™ *catalyst production*



TEM for fresh Auro*lite*™ *catalyst*

Gold Meeting in Texas

A meeting entitled 'Recent Advances in Catalysis by Gold' took place at Texas A&M University on May 16 2008. The talks included 'Nanoporous architectures for self-healing Au catalysts' by Prof Abhaya Datye, University of New Mexico; 'Gold catalysed oxidation reactions in liquid water' by Prof Robert Davis, University of Virginia; 'Catalysis by highly dispersed supported gold: evidence of catalysis by isolated gold cations and by gold nanoclusters', by Prof Bruce Gates, University of California, Davis; 'Morphology of the active site; from Au clusters to Au films', by Prof Wayne Goodman, Texas A&M University; 'Aberration corrected analytical electron microscopy studies of gold-based catalysts, by Prof Chris Kiely, Lehigh University; 'Control of dimensionality, structure, and reactivity of gold nanocatalysts; 2D or not 2D?', by Prof Uzi Landman, Georgia Institute of Technology; and 'The Water-Gas Shift on gold-oxide catalysts: active sites and reaction mechanism' by Dr Jose Rodriguez, Brookhaven National Laboratory ■

If you have a contribution for CatGold News please email industry@gold.org

A Noble Cause: Modern Gold and Platinum Group Catalysis

A well organised meeting took place in London on Wednesday 16 April 2008: there were 6 talks on homogeneous catalysis by gold and the platinum group metals; and the 4 on gold showed that soluble gold compounds are especially versatile for synthesising new organic pharmaceuticals and gold's unique capabilities in this regard, based on its maximum relativistic effect, mean that some organic compounds have only been synthesized using gold catalysts. The titles of the four gold talks were: 'Molecular Gold Catalysts for Organic Synthesis' by Prof Stephen Hashmi, Heidelberg, Germany; 'Gold: An Old Metal for New Chemistry' by Dr Fabien Gagosz, Ecole Polytechnique, Palaiseau, France; 'Gold-Catalysed Skeletal Rearrangement of Enynes and Beyond' by Prof Antonio Echavarren, ICIQ, Tarragona, Spain; and 'Gold(I) Catalysts for Organic Synthesis: Development, Applications and Enantioselective Catalysis' by Prof Dean Toste, University of California, Berkeley, USA.

High turnover numbers and turnover frequencies have been demonstrated in some of the gold-catalysed reactions but this was not a prominent aspect of the investigations which had mostly been done on a small scale, eg in NMR tubes; and it was emphasized that many of the gold-catalysed reactions could be conducted in the open lab since they were not sensitive to the presence of water or oxygen. Gold's resistance to sulfur-poisoning in these situations was also apparent since organic transformations of sulfur-containing compounds were demonstrated ■

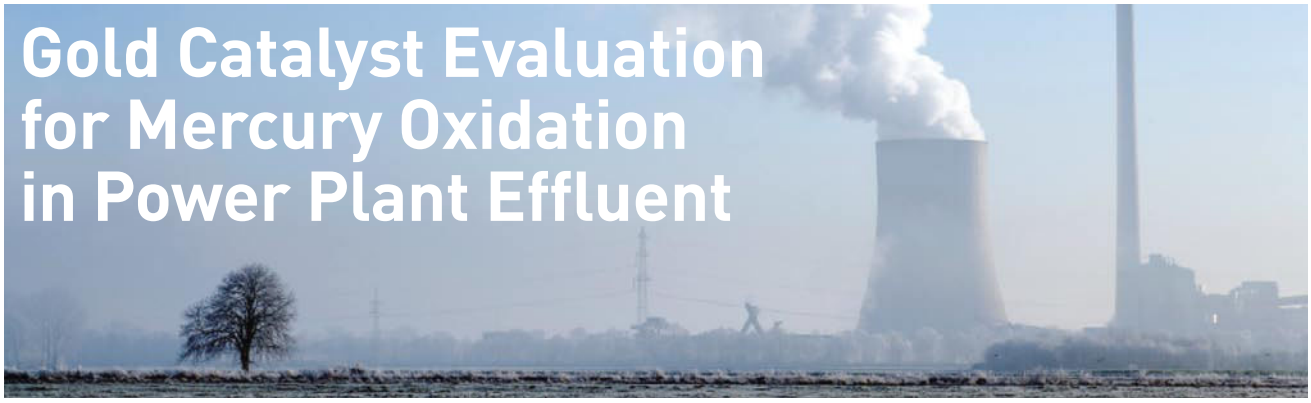
Interactions between Gold and Halogens

The chemical inertness of gold nanoparticles is being increasingly challenged, and could explain aspects of activity and poisoning of gold catalysts.

In a paper on CO oxidation (Understanding the effect of halide poisoning in CO oxidation over Au/TiO_2, SM Oxford, JD Henao, JH Yang, MC Kung and HH Kung, *Appl Catal A: Gen*, 2008, **339**(2) 180-186) halide was shown to prevent the full reduction of cationic Au. On reduced Au samples bromide was preferentially adsorbed on Au and not on TiO_2. Not all adsorption sites are catalytically active: the perimeter Au atoms at/near the particle interface are active, and halide selectively poisons the catalytic sites. These results add valuable additional insight into the Bond-Thompson reaction mechanism.

In the JACS paper (Nature of Cl bonding on the Au(111) surface: evidence of a mainly covalent interaction, TA Baker, CM Friend and E Kaxiras, *J. Am. Chem. Soc.*, 2008, **130**, 3720 – 3721), DFT calculations show that the bonding between Cl and Au is primarily covalent in character: this is exceptional because most halogens bind to metal surfaces via ionic interactions. Gold's high electronegativity makes it the most likely transition metal to form a covalent bond with highly electronegative elements such as chlorine. The special nature of this bonding with gold should be taken into account when thinking about the effect of the presence of chloride on gold particle sintering/poisoning and homogeneous catalysis using $AuCl_3$ etc ■

Gold Catalyst Evaluation for Mercury Oxidation in Power Plant Effluent



Under a Phase III award, URS Corporation, Austin, Texas, USA is commencing a full-scale field test of a gold-based Hg^0 oxidation catalyst at Lower Colorado River Authority's Fayette Power Project Unit 3 in Spring 2008, to assess its suitability for use in treating effluent from coal-based power plants. The test is intended to confirm the required catalyst quantities and catalyst life for achieving an average of 70% or greater Hg^0 oxidation in PRB (Powder River Basin) coal-based plant flue gases over a two-year period. The project represents the next logical advancement of the catalytic oxidation technology from its current pilot-scale.

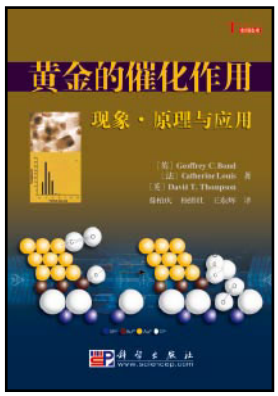
It will answer technical questions such as the catalyst quantity required to achieve high Hg oxidation percentages, catalyst life, the efficiency of catalytically-oxidized Hg capture in full-scale wet FGD (flue gas desulfurization) systems, and the ability to keep the catalysts clean of fly ash buildup at full-scale with sonic horns.

For further information, see: http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/pubs/netl%20Hg%20program%20white%20paper%20FINAL%20Jan2008.pdf

Chinese translation of 'Catalysis by Gold'

The great potential and bright future for gold in various aspects of catalysis science and technology have been encouraging many chemists, especially young people, to consider new opportunities in catalysis. The book 'Catalysis by Gold', by Geoffrey C Bond, Catherine Louis and David T Thompson, published by Imperial College Press in August 2006, presents a comprehensive discussion on the topic and provides a systematic review of the most important features of gold catalysts, in ways that not only meet the interests of skilful researchers but also help beginners and students to achieve a better understanding of this ever growing topic.

The team of translators: Dong-Hui Wang (left), Jie Yu, Yi Zuo, Bo-Qing Xu, Hui Shi and Xu-Zhuang Yang (right)



Studies of catalysis by gold have now evolved as an important topic of catalysis research in China since the beginning of this new century. Aiming to seek catalysis solutions for the country to sustain her energy, environment and chemical conversion technologies, the catalysis community in this biggest country by population has grown to involve more than 3000 researchers with a very high percentage (ca 80%) being under the age of 40. In order to provide better assistance to those of our young colleague researchers and graduate students to understand systematically the fundamentals and potential of gold catalysts and to catch up with the up-to-date references on the topic, Drs. Dong-Hui Wang, Xu-Zhuang Yang and I decided towards the end of 2007 to produce a Chinese version of the book 'Catalysis by Gold'. The Chinese translation is expected to be published by early August 2008 by the Science Press of China (Beijing). We would anticipate that this will lead to an even greater research interest in rational exploration, understanding and application of gold catalysts in China.

Bo-Qing Xu, Tsinghua University, Beijing