WORLD GOLD COUNCIL

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CatGold NEWS

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

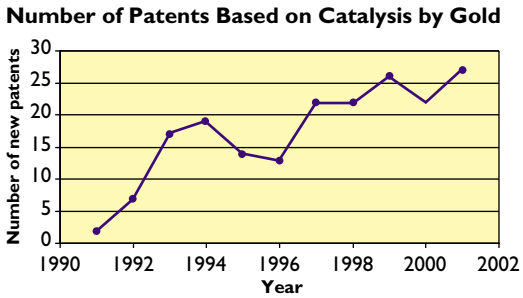
There are some exciting news stories in this Spring Issue of CatGold News!

We have the very latest news on the World Gold Council's Reference Catalysts which will be manufactured by Süd Chemie, Japan and should provide excellent research opportunities later in the year. We very much look forward to supporting the distribution of these catalysts to interested organisations. There are sure to be results on this subject presented at the Gold 2003 Conference, the latest news of which was just released at the time of going to press. Please make a note of the provisional date in your diary now.

At the World Gold Council offices, we were also encouraged to note that a recent review of filed patents based on gold catalysis, revealed a surprisingly high level of activity from both academic and industrial organisations. One such application could be in fuel cells, and in this issue we have some views on this particular topic from Don Cameron of the Interact Consultancy.

Enjoy this issue and keep sending us relevant news for the next issue of CatGold News, to be published in the autumn, later this year.

Golden Age for Catalyst Patents



The number of patents related to gold catalysis appears to be on a long term upward trend, with 27 patents granted during 2001. In the last 10 years, around 50 industrial companies worldwide have successfully applied for patents in this area. Based on analysis by World Gold Council, the focus of the patents was approximately split by subject in the following way: Chemical Processing ~46%, Pollution Control ~29%, Catalyst Manufacture/Regeneration ~15%, and Fuel Cells ~10%.

For further information or if you have news of the industrial commercialisation of the technologies related to these patents, please contact World Gold Council. A listing of patents related to gold catalysis now appears on the Council's website www.gold.org under the Science and Industry Section (Gold Catalysis) ■

Reference Gold Catalysts – UPDATE

Following the announcement in our previous issue, World Gold Council has taken the initiative in commissioning the preparation of a number of reference gold catalysts. Three of these will be gold on oxide supports to be made by Süd Chemie, Japan under the supervision of Dr Masatake Haruta, with characterisation at AIST, Japan.

The fourth is likely to be gold on carbon and the choice of support is currently being made via evaluation work carried out in collaboration with Professor Michele Rossi of the University of Milan. The catalysts, which should be available by November 2002, are indicated in the Table.

Catalyst Type	*Method*
1) 3wt%Au/TiO_2 (P25)	**Deposition Precipitation**
2) 0.3wt%Au/Fe_2O_3 on alumina beads	**Deposition Precipitation**
3) 5wt%Au/Fe_2O_3	**Coprecipitation**
4) 10wt%Au/C (Cabot XC72R)	**Gold Sol**

The details of the catalyst preparations will be provided and the catalysts (1-3) will be characterized with respect to gold loading, gold particle size and catalytic activity in carbon monoxide and hydrogen oxidation tests. For catalyst 4, appropriate characterisation and reactivity data will also be provided.

The merits and effective use of reference catalysts are described by Professor Geoffrey Bond in his accompanying letter in this issue. It will be a condition of supply that recipients of these catalysts share their results both in the characterization and activity spheres, and WGC will be pleased to publish these results in Gold Bulletin. The results will also be presented at future conferences on gold catalysis.

Comments on how best to make this WGC reference catalyst project most useful to people involved in research on and practical applications for gold catalysts are very welcome ■

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Report on the Au/Ag Symposium

Professor Mayfair Kung delivering her talk during the Au/Ag Symposium

The excitement which has been generated by the new results in gold catalysis was clearly evident from the large attendance at the Symposium on Gold/Silver Catalysis, taking place 3–5 September 2001, as part of EuropaCatV meeting in Limerick, Ireland.

Industrial interest

Following the Catalytic Gold Conference in South Africa in April 2001, this was the second major international conference on gold catalysis to be held in 2001: a clear indication of the new interest being developed by the recent advances in the subject. This meeting consisted of four half-day sessions, and a poster session on the Tuesday evening. All five sessions were well attended, with between about 70 and over 200 participants being present at all the sessions. Along with the participants from academia, there were also a significant number of industrial personnel present and it became clear during the discussions that a number of industrial organizations are assessing the catalytic properties of gold, and this is supported by increased patent activity, (see also page 1).

Keynote lecture

In the keynote lecture on 'The Current Status of Catalysis by Gold', Professor Graham Hutchings (Cardiff University) pointed out that there has been a renaissance of interest in the use of gold as a catalyst in reactions relevant to both chemical processing and pollution control. Reactions include carbon monoxide oxidation, water gas shift, hydrochlorination and selective hydrogenation. This talk was illustrated by examples where supported gold has been demonstrated to be the best catalyst. The importance of gold particle size and other physical and preparative variables was indicated.

Cape Town Conference

Both the earlier Cape Town Conference, 'Catalytic Gold 2001', and the Limerick meetings included papers on homogeneous and liquid and gas phase heterogeneous gold catalysis research. Limerick also had a paper on electrocatalysis by gold and silver (A.J. Ahern, L.D. Burke, L.M. Hurley and A.P. O'Mullane, University College of Cork, Ireland), a topic which also promises to have special and useful features with potential applications. The highlights of both the Cape Town and Limerick meetings have been reported in *Gold Bulletin*, 2001, **34**, 56 - 66 and 134 - 140 respectively ■

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GOLD 2003
NEW INDUSTRIAL USES FOR GOLD

GOLD 2003 – VANCOUVER !

At the time of going to press, planning for the follow up to the Catalytic Gold Conference held in South Africa during April 2001, was underway. At this initial stage of planning, the conference is likely to have four themes: Gold Catalysis, Nanotechnology, Materials and Chemistry. The likely conference date is week beginning the 29 September 2003, Vancouver, Canada. We hope to confirm this shortly, but pencil this date in your diary now ! ■

Vancouver – the Gold 2003 venue

Points of View

'REFERENCE' GOLD CATALYSTS

I was delighted to learn that it had been decided to commission one or more 'reference' gold catalysts and to make them available to the scientific community.

In 1976 during the Sixth International Congress on Catalysis in London, a group of European scientists met under the chairmanship of Professor Eric Derouane, and decided to initiate programmes of work employing 'standard' or 'reference' platinum and nickel catalysts. The former was a 6.3% Pt/SiO_2 (EUROPT-1) and was made by Johnson Matthey; the latter was 20% Ni/SiO_2 and was made at the University of Utrecht. A commercial platinum reforming catalyst (0.3% Pt/Al_2O_3, EUROPT-3) was added later. I was privileged to participate in this programme, which I found extremely useful.

The EUROPT-1 in particular has been thoroughly characterised and widely studied; it is still available and is still cited in the literature. It has proved invaluable in (i) the calibration of apparatus for measuring metal dispersion and catalytic activity, particularly of the home-made variety; (ii) finding out what conditions of pre-treatment were needed to give results that were reproducible from one laboratory to another; and (iii) not least important – training new research students in proper techniques and procedures.

The availability of a great deal of information of all kinds *on the same catalyst* has also been of immense benefit in helping to understand how catalysts work. One of the great problems with the literature on catalysis is that so many people make their own catalyst, and characterise and use it in a very limited way, making comparison between different studies almost meaningless. The same sort of problem is already visible in catalysis by gold; taking the well-known oxidation of carbon monoxide as an example, we have seen that not only are home-made catalysts necessarily used, but also that they are tested under one particular set of conditions that differ from one laboratory to another. It is impossible to tell reliably from such work what parameters are actually relevant to catalytic activity.

I therefore hope that the advent of the 'reference' gold catalysts will help to improve this situation, and that they will be included as a point of reference in all research on gold catalysis. I strongly commend this initiative, and trust that the material when available will be widely employed ■

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Research on Gold Catalysis in South Africa

Three groups in South Africa are engaged in research on heterogeneous catalysis by gold. Two of the groups are within local universities, while the third is at a national research institute.

Research at the University of the Witwatersrand (M S Scurrell, N J Coville) into gold catalysis started during the late 1980's. Recent efforts have focussed on structure/activity relationships, particularly for reactions of environmental concern such as CO oxidation, total hydrocarbon oxidation and the water gas shift reaction. Characterisation methods available include chemisorption, DRIFTS, TPR, XPS, ^{197}Au Mossbauer spectroscopy, HRTEM and XRD. The group attempts where possible to perform characterisation work in as near an *in situ* manner as possible. The detailed interaction between CO and NO on gold surfaces has been investigated using DRIFTS methods.

> "The research at Mintek forms part of Project AuTEK, and is led by Elma van der Lingen and Mike Cortie"

The most recent work has examined relatively unconventional methods for preparing gold catalysts, with some of the less well studied supports, including zeolites, MCM-type materials and mixed oxides. Sol-gel methods are also being studied – an approach not widely used to date for gold systems. Application of infrared spectroscopy to studies of metal carbonyls adsorbed on gold surfaces is proving of use in monitoring the electronic environment of surface gold in solids and experimental work is being backed up using Density Functional Theory (DFT).

The Catalysis Research Unit within the Department of Chemical Engineering at the University of Cape Town has been involved in heterogeneous catalysis for over 20 years. The inclusion of gold as a topic of investigation, is however, only recent and is being driven by Jack Fletcher and Eric van Steen. The first activities started in 2000. Since that time one MSc(Eng) degree has been awarded (gold catalysed water-gas shift conversion) and two further MSc degrees will be completed in 2002 (molecular modelling of gold catalysed methanol synthesis and the activity of gold catalysts for selective olefin hydrogenation). A PhD study of both theoretical (molecular modelling) and experimental aspects of gold catalysed methanol synthesis will start during the year.

Project AuTEK members. Front: Diandree Padayachee, Iris Klingbiel, Elma van der Lingen, Herman Schwarzer. Back: Gaby Steinbach, Gary Pattrick, Stephen Roberts, Edson Muhuma, Mike Cortie

Potential for Further Improvement

Findings to date suggest that the Au/ZnO system is rather active for the low temperature water gas shift conversion, a finding not previously reported in the literature. Moreover, at typical industrial LTS feed composition and conditions of 185 - 220°C, 20 - 30 bar, molar steam/CO ratios of 0.5 - 1.5 and dry gas space velocities of 5000 - 10000 SGHSV, the catalyst appears stable over 200 hours on stream. As gold dispersion and particle size was not optimal, there exists substantial potential for further improvement of the system. As to gold catalysed methanol synthesis, the following results have been determined via molecular modelling, *viz* i) that cationic Au is necessary for the synthesis to proceed to completion and, ii) that as opposed to the methoxy intermediate present for the copper catalysed reaction, a hydroxyl methyl intermediate exists in the case of the Au catalysed synthesis.

Both university groups are partners in a new initiative involving collaborative research in gold catalysis with five research centres in the USA.

Specific Applications

The research at Mintek forms part of Project AuTEK, and is led by Elma van der Lingen and Mike Cortie. Project AuTEK is a joint initiative between AngloGold, Gold Fields, and Mintek and addresses all industrial applications for gold, not just catalysis. The catalyst part of AuTEK focuses on the use of gold for specific application fields. For the use of gold catalysts for improving air quality the emphasis is on the oxidation of CO at room temperature. The development of gold-based catalysts for the reduction of NOx for lean-burn applications is a collaborative project between South Africa, The Netherlands and France. The group also investigates the use of gold-based catalysts for the chemical processing industry. Novel preparation techniques have been developed and the catalytic activity of gold on single and mixed metal oxides with and without promoters is being investigated. The allocation of bursaries to students at the University of Cape Town and the University of the Witwatersrand forms part of Project AuTEK ■

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GROW–

Funding for Feasibility Studies in Gold Catalysis

Last year, World Gold Council announced its GROW programme providing limited funds to support short term R and D projects on the science and technology of gold and its applications. Project proposals related to gold catalysis are invited for 2002. Guidelines of the programme are available from the Council's website, at www.gold.org under the Science and Industry Section. In general, World Gold Council have a preference for catalysis submissions based on feasibility studies related to commercially relevant reactions, rather than fundamental scientific research. For further details please contact

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People on the move

Chris Kiely, currently Professor of Materials Chemistry, University of Liverpool will be taking up a new appointment as Professor of Materials Science and Engineering at Lehigh University, Pennsylvania USA in July 2002.

People

Professor Graham J Hutchings
Head of Chemistry,
Cardiff University

Graham Hutchings is one of the founding fathers of gold catalysis. Whilst working for AECI in South Africa during 1985, he was the first researcher to predict that gold would be the most active heterogeneous catalyst for reactions of alkynes, including the addition of hydrogen chloride to acetylene to produce vinyl chloride.

He has since continued his interest in gold catalysis and has demonstrated that small gold particles can be effective and selective hydrogenation catalysts and that, furthermore, gold can be electronically promoted by the addition of low concentrations of sulfur.

More widely, Graham has an international reputation in the field of heterogeneous catalysis, particularly for the study of oxides and oxidation reactions. In 2001, he published 25 papers on heterogeneous catalysis and, since becoming an academic researcher in 1984, he has published over 370 papers in this field. Graham was Deputy Director and Professor at the Leverhulme Centre for Innovative Catalysis, University of Liverpool before moving to his current position as Professor of Physical Chemistry and Head of the Chemistry Department at Cardiff University. His research has received much attention, including the award of the 1996 Distinguished Langmuir Lectureship of the American Chemical Society and, in 2001, he was awarded the DGMK-Kolleg 2001 Lectureship by Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle (DGMK German Society for Petroleum and Coal Science and Technology). He has given many plenary and invited lectures at major international conferences and, in 2001, gave keynote lectures on the emerging topic of Gold Catalysis at the first major international conference 'Catalytic Gold 2001', held in Cape Town and at the EuropaCat V Conference in Limerick.

Graham lives on a small farm overlooking Symond's Yat, a UK beauty spot and, away from work, he enjoys good food, wine and conversation ■

New Opportunities for Gold Catalysts in Fuel Cells

Fuel cell electric power generators are entering commercial service in a number of programmes worldwide. They exhibit high efficiency combined with low pollutant emissions, and can be built in a wide range of sizes to power laptop computers, provide heat and power for individual homes, or district schemes. Transport systems vary in size from electrically driven scooters through passenger vehicles to municipal buses. Fuel cells operate by electrochemical oxidation of hydrogen or hydrocarbon fuels, the low temperature types requiring expensive platinum metals catalysts. The most advanced low temperature systems incorporate solid polymeric electrolyte and consume hydrogen.

Considerable effort is in progress to perfect compact reactors capable of generating pure hydrogen for stationary systems and vehicles. Most of these incorporate a reforming stage for hydrocarbon fuel followed by the water gas shift reaction to yield hydrogen rich gas mixtures. Unfortunately these also contain a small proportion of carbon monoxide, which acts as a platinum catalyst poison in the fuel cell, and steps must be taken to remove this contaminant. Several recent papers have indicated that gold catalysts on oxide support materials can selectively oxidize carbon monoxide at low temperatures to create hydrogen streams containing very low levels of carbon monoxide. The water gas shift reaction is itself catalysed by oxide-supported gold at lower temperatures than those used with the current commercial catalysts.

Even though they have been used for many years in specialised low temperature alkaline electrolyte fuel cells, gold catalysts have not been widely investigated. There is evidence that pure gold has electrocatalytic activity in a wide range of applications, as well as forming alloys with the platinum group metals. In particular, the electrocatalytic properties of highly dispersed small particles are largely unexplored.

Hence there are at least two areas in fuel cell technology with potential for using gold catalysts: in the formation and clean-up of hydrogen fuels, and as constituents of the fuel cell electrodes. In addition, the excellent corrosion resistant properties of gold could lead to other applications in the demanding environment of the fuel cell ■

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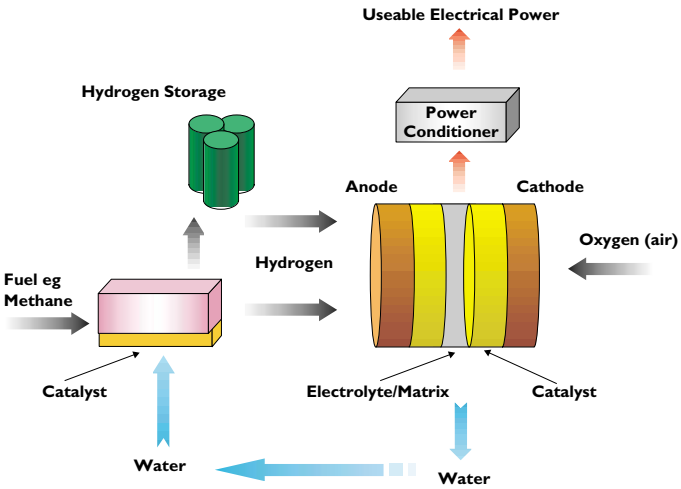

Basic Principle of Fuel Cell

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