Hydrodechlorination of 1,1-dichloroethene (DCE) in water was followed in situ using SERS with Pd islands grown on Au-nanoshell films (‘Observing metal-catalysed chemical reactions in situ using surface-enhanced Raman spectroscopy on Pd-Au nanoshells’, KN Heck, BG Janesko, GE Scuseria, NJ Halas and MS Wong. J Am Chem Soc. 2008, 130, 16592). Development of this new technique for observing aqueous systems provides mechanistic evidence for the results of significant Au-enhancement for Pd-catalysed hydrodechlorination of DCE, trichloroethene (TCE), and perchloroethene (PCE), all common water pollutants. The evidence obtained supports a sequence of dechlorination and hydrogenation steps for DCE, TCE and PCE and other related contaminants when using Pd-Au nanoparticle catalysts.

Hydrodechlorination of chlorinated water pollutants

Synthesis of azo compounds using environmentally friendly route

Aniline has been reported to be converted to azobenzene in >98% yield using 1.5%Au/TiO₂ in toluene at 100°C and 5 bar initial oxygen pressure (‘Gold-catalysed synthesis of aromatic azo compounds from anilines and nitroaromatics’, A Grirrane, A Corma and H Garcia, Science, 2008, 322, 1661 – 1664). Conversions of 100% and selectivities of up to 98 and 92% have been obtained using 1.5% Au/TiO₂ and 1.44%Au/CeO₂ respectively.

Azobenzene can also be synthesized from nitrobenzene using a two-step process in which hydrogen at 9 bar and 120°C is used in the first step to give aniline and then oxygen at 5 bar to give azobenzene, each stage having a selectivity of ca 95%.

Aromatic azo compounds are high-value chemicals widely used in industry as dyes, pigments, food additives and drugs and their preparation currently requires stoichiometric quantities of environmentally unfriendly transition metals or nitrites. The efficient conversion of a wide range of nitroaromatics into azo compounds using this new green route is confidently predicted.
A nationwide research project is ongoing!

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In Japan there are two major government research funding organizations. One is NEDO (New Energy and Industrial Technology Development Organization) which belongs to the Ministry of Economy, Trade and Industry. Another is JST (Japan Science and Technology Agency) which belongs to the Ministry of Education, Culture, Sports, Science and Technology. In principle, the former supports challenging R&D in industries for starting-up new technology business, while the latter focuses on fundamental research that may bring new seeds for the next-generation technology.

A research project entitled 'Catalyst Design of Gold Clusters through Junction Effect with Metal Oxides, Carbons, and Polymers' started as one of the research projects in the research area of Development of the Foundation for Nano-interface Technology in the CREST (Core Research for Evolutional Science and Technology) program in October 2006. The project will continue until March 2012 (five and a half years), subject to review, when the total direct research funding will exceed 420 million Japanese Yen (about 3.5 million EU, except for 30% overheads).

A unique aspect of this project is that it focuses on gold clusters smaller than 2 nm in diameter (<300 atoms) where their electronic nature changes from that of bulk gold. Ten research groups represented by the following scientists are collaborating with each other.

1. Catalyst preparation: size control, combination with organic complexes and metals

1) Tatsuya Tsukuda (Catalysis Research Center, Hokkaido Univ.)
Precise size control of gold clusters stabilized by PVP at around 1 nm by using a micro-mixer and the aerobic oxidation of alcohols
2) Katsuaki Konishi (Graduate School of Environmental Earth Science, Hokkaido University)
Thioether-stabilized 55 atoms gold clusters encapsulated by manganese porphyrin and the oxidation of olefin and glucose
3) Naoki Toshima (Graduate School of Science and Engineering, Tokyo University of Science, Yamagichi)
Preparation of gold alloy clusters (Pt/Ag/Au) in aqueous solution and glucose oxidation

2. Structure analyses, theoretical calculations, and surface sciences

1) Tomoki Akit (Research Institute of Ubiquitous Energy Devices, AIST)
HR-TEM study of gold clusters supported on metal oxides
First Principle calculation of the bonding energy of gold clusters in contact with metal oxides having different surface stoichiometries
Reactions of laser-ablated gold atoms and deposition of gold clusters on MOF (metal organic framework)
Desulfurization by adsorption- thermal desorption over supported gold catalysts
2) Yoshiaki Kido (Department of Physics, Ritsumeikan University)
Evaluation by high-resolution ion scattering and others of electron distribution at gold- metal oxide interfaces as a function of gold cluster size
3) Tadahiro Fujitani (Research Institute of Innovation in Sustainable Chemistry, AIST)
Preparation of model supported gold catalysts for a mechanistic study of adsorption and reaction
4) Mitsutaka Okumura (Department of Chemistry, Osaka University)
Quantum chemistry calculation of adsorption properties of gold clusters

Gold catalysis in Japan

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3. Catalyst development

1) Makoto Tokunaga (Department of Chemistry, Kyushu University)
Applications of supported gold clusters to organic syntheses, for example, hydroformylation of olefins\textsuperscript{11} and one-pot syntheses

2) Yasuo Iizuka (Kyoto Institute of Technology)
Direct deposition of gold clusters on metal carcogenides\textsuperscript{12} and studies of CO oxidation mechanisms

3) Masatake Haruta (Graduate School of Urban Environmental Science, Tokyo Metropolitan University)
Direct deposition of gold clusters on carbons and polymers\textsuperscript{13}
Applications of gold clusters to propylene epoxidation and biomass-related chemistry\textsuperscript{14}

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Members of the Gold Catalyst Team for the Research Program of Core Research for Evolutional Science and Technology, Japan Science and Technology Agency: Hiraizumumi on 27th October, 2007
RSC reviews on gold, including catalysis

A recent issue of Chemical Society Reviews is devoted to the chemistry of and catalysis by gold. The introduction and some of the heterogeneous catalysis papers are summarized below:

**Gold – an introductory perspective**, GJ Hutchings, M Brust and H Schmidbaur, Chem Soc Rev, 2008, 37, 1759 – 1765

This is the introduction to a thematic issue containing reviews on gold catalysis, gold chemistry, gold nanotechnology and theoretical aspects of gold chemistry. There are sections indicating some remaining challenges and opportunities for the future, including commercial applications.

**Catalytically active gold on ordered titania supports**, M Chen and DW Goodman, Chem Soc Rev, 2008, 37, 1860 – 1870

This discusses the unique properties of Au/TiO₂ catalysts for carbon monoxide oxidation. It is claimed that an Au bilayer nanofilm, two atomic layers thick, exhibits unusually high activity for carbon monoxide oxidation. The thickness of a gold particle is more significant than its diameter wrt its catalytic activity, but the TOF is greatest at ca 3nm.

Cationic gold may be an active species but less active than metallic gold: in the Bond-Thompson mechanism it was also proposed that both species contribute to the activity.

**Catalysis by gold dispersed on supports: the importance of cationic gold**, JC Fierro-Gonzalez and BC Gates, Chem Soc Rev, 2008, 37, 2127 – 2134

Catalysis by cationic gold takes place both in solution and on surfaces. The relative importance of cationic gold and gold clusters in supported catalysts for carbon monoxide oxidation is still unclear.

**Selective oxidation using gold**, C Della Pina, E Falletta, L Prati and M Rossi, Chem Soc Rev, 2008, 37, 2077 – 2095

Useful wide-ranging review (with 168 references) of selective oxidation reactions with examples of stable, selective gold catalysts, emphasizing advantages of gold over other metal catalysts. The need for kinetic investigations to provide a better definition of mechanisms is recommended.

**Supported gold nanoparticles as catalysts for organic reactions**, A Corma and H Garcia, Chem Soc Rev, 2008, 37, 2096 – 2126

It is stated that gold nanoparticles provide a bridge between homogeneous and heterogeneous catalysis. This comprehensive review (with 282 references) contains sections on catalyst preparation, addition to multiple C-C bonds, rearrangements, C-C coupling, cyclization, oxidation, selective hydrogenation, radical reactions initiated by gold nanoparticles, and gold in environmental catalysis (eg VOC oxidation).

**Highlights of CATSA 2008, Parys, South Africa 9-12 November 2008**

There were some 250 participants at this very exciting meeting on recent developments in catalysis. The keynote talks were all stimulating, all the plenary talks contained valuable material and the standard of the student presentations was excellent. The enthusiastic and friendly atmosphere generated by the many pleasant social opportunities made this a memorable meeting and the organising committee should be congratulated on their appropriate selection procedures and organizational competence!

**Talks and posters**

There were a number of contributions principally on gold catalysis, and its importance was emphasized in other presentations. Titles of the gold presentations were as follows:

**Talks**

**Testing of carbon supported gold catalysts using glucose oxidation**, Brendan Beeming, University of Cape Town, described how gold supported on fishbone carbon nanotubes were made by ion exchange. 10nm gold particles were the most active.

**Methane reforming with CO₂: a study on surface carbon species**, Laszlo Guczi (Budapest, Hungary), indicated the advantages of adding gold to NiMgAl₂O₄ catalyst for methane dry reforming with 30%CO₂ present (as in natural gas in Hungary). The presence of Au-induced lower light off temperatures prevented carbon formation on the catalyst and made the catalyst more durable.

continued on next page
An investigation of ion exchange as a method for preparation of gold catalysts for use in ethylene glycol oxidation, Jenni Case, University of Cape Town, indicated where ion exchange was used to obtain small well dispersed gold particles, and the resulting catalysts gave high selectivity to glycolic acid.

Low temperature oxidation of ethanol to acetic acid using gold-based catalysts, Steton Tembe, University of Witwatersrand, had recorded high yields of acetic acid using AuTEK scaled-up catalysts.

The effect of preparation method on the photocatalytic behaviour of Au/TiO₂ catalysts, John Moma, Project AuTEK, described experiments which demonstrate that titania is photochemically active, but to date the addition of gold has not improved this activity, as claimed in the literature.

Other presentations where catalysis by gold was relevant:

The use of precious metals in synthesis gas generation and Fischer Tropsch catalysis, Martin Fowles, Johnson Matthey Catalysts, Billingham, UK, indicated that addition of Pt to cobalt FT catalysts brought benefits, as did ruthenium, iridium and rhenium, but Pt was the only serious contender of these due to the limited supplies of the other metals. If gold produced similar effects, the supply position would not be a problem and this would be a major opportunity for a new use of gold. The use of Au in Fischer Tropsch is described in the paper by K Jalama, NJ Coville, D Hildebrandt, D Glasser, LL Jewell, JA Anderson, S Taylor, D Enache and GJ Hutchings, Topics Catal, 2007, 44, 129.

Methane activation and conversion on solids: are we making progress?, Prof Mike Scurrell, Wits University, RSA, gave a realistic but optimistic survey of the various approaches which have been made over the years. Two opportunities for gold were indicated. The first was a report that Au/CaO-La₂O₃ gave a high selectivity to benzene, and the second was that Au-Pd catalysis could be used to generate hydrogen peroxide in situ to be used in conjunction with Fenton reagent to give alcohols.

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People profile

Dr Catherine Louis
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Catherine is Director of Research of the CNRS at UPMC in Paris. Previously, she studied chemistry at the Université Denis Diderot (Paris 7), then obtained an Engineering Diploma at the Ecole Supérieure de Physique et Chimie Industrielle in Paris. Following this she studied the preparation and reactivity of highly dispersed supported molybdenum oxide catalysts under the direction of Prof Michel Che at the Université Pierre et Marie Curie for which she received her PhD degree in 1985. At that time, she was already full time researcher of the CNRS (Centre National de la Recherche Scientifique). After a 20 month post-doctoral period in Prof Alex Bell’s Laboratory in the University of California at Berkeley, in 1986-88, working on coupled CO thermodesorption and infrared characterisation of supported ruthenium catalysts, she then moved back to Paris. Here she started research into the preparation of various supported metal catalysts, studying the nature of the precursors, the procedure of preparation (such as impregnation, cation adsorption, deposition-precipitation), and the conditions of drying and activation, with the goal of controlling metal or oxide dispersion on oxide supports based on detailed investigation of the chemical phenomena occurring during catalyst preparation.

Since 2000, she has been working on gold catalysts, studying their preparation with the objective of controlling the parameters so as to achieve small gold particles on various oxide supports with a 100% yield of gold deposition, and on their catalytic properties in oxidation (CO, VOC), deNOx, and selective hydrogenation reactions.

In collaboration with Geoffrey Bond and David Thompson, she participated in the writing of the first book on catalysis by gold (2006), which has already been reprinted (2007) and translated into Chinese (October 2008).

In France, she is very active in the promotion of gold nanoparticles in various fields of biology, chemistry and physics, within the framework of a CNRS network entitled ‘or-nano’ (nano-gold) (www.or-nano.org).

Catherine is the head of one of the four research groups of the laboratory, which comprises 6 permanent researchers.

In spite of her fascination with gold nanoparticles, she prefers silver jewels! Her interest in science and research is balanced by leisure-time interests in scuba-diving, swimming, sailing and literature, art exhibitions, cinema and theatre.

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Also available ‘Gold Catalysis in Southern Italy’ by Leonarda Liotta can be found on page 66.