

Conference Report

Gold Catalysis Highlights at EuropaCatVIII in Turku/Åbo, Finland, August 26 – 31, 2007

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Attendance at this conference was around 1,500 delegates from 56 countries. The major European countries, France, Germany, Italy, Spain and the UK were strongly represented but other European countries including Finland also had significant numbers of delegates and Japan and Russia were well represented. Catalysis by gold had a strong presence with 59 posters and 15 talks scheduled on various aspects of this topic. Project AuTEK collaborated with the World Gold Council to present an exhibition stand demonstrating the opportunities for applications for gold and gold alloy catalysts, and this stimulated a lot of interest and lively discussions. A short report on the high profile of gold catalysis within this conference is included in the *CatGold News* section of this issue.

Reports with potential for commercial applications

A keynote talk entitled 'Gold nanoparticles for catalysis' was presented by Catherine Louis, UPMC, Paris, co-author of a recent book on gold catalysis (1). She indicated that gold nanoparticles have different properties from bulk gold and for example the colour (red/purple) is different from that of bulk gold as a result of surface plasmon resonance. The increasing number of surface atoms as the gold particle size decreases to < 5 nm, possibly in combination with specific electronic properties, imparts a surface reactivity to gold nanoparticles, and this means that catalytic activities in such reactions as carbon monoxide oxidation increase as the particle size decreases.

The production of vinyl acetate using Au-Pd catalysts is a well-established commercial process, and other potential industrial applications for gold and gold alloy catalysts have been patented and show promise: these include their use in respirators for protection from CO poisoning, removing CO and trace amounts of VOCs and ozone from living areas, and use of Au-Pd-Pt catalysts for diesel exhaust emission control. Hydrodechlorination of trichloroethene, the total oxidation of

VOCs and in water (Catalytic Wet Air Oxidation, CWAO) and the direct synthesis of hydrogen peroxide from oxygen and hydrogen are catalysed effectively by Au-Pd or Au.

Chemical synthesis reactions such as glucose to gluconic acid, propene to propene oxide, production of methyl glycolate from ethylene glycol, and the selective oxidation of alcohols to aldehydes are all catalysed by gold and/or gold/PGM alloys. Alkynes and alkadienes can be successfully removed from alkene streams used for polymer production by selective hydrogenation with gold catalysts, and CO can be selectively oxidised in the hydrogen streams used for PEM fuel cell operations. The water-gas shift is also catalysed by gold at lower temperatures than commercial catalysts. Homogeneous catalysis by gold has been demonstrated to have unique chemical synthesis opportunities.

Applications for gold catalysts were also highlighted in many of the other talks and posters. For example, M Mimura, AIST, Tsukuba, Japan described work on the preparation of propene oxide from propene using O_2/H_2 and a gold on titanosilicate catalyst, and Peter Haider, ETH, Zurich described 'Gold supported on Mg-, Al- and Cu-containing mixed oxides: structural properties and behaviour in catalytic aerobic oxidation' where TOFs of up to 1300 h^{-1} and selectivities of $\geq 98\%$ had been recorded for the liquid phase oxidation of various structurally different alcohols.

Graham Hutchings, Cardiff University, UK, described work on 'Nanocrystalline cerium oxide produced by supercritical antisolvent precipitation as a support for high activity gold catalysts', where the resulting Au/CeO₂ catalyst had a higher activity for CO oxidation under ambient conditions than a similar catalyst prepared from CeO₂ obtained in a conventional manner by thermal decomposition of the acetate (2); and Silvio Carrettin, ITQ, Valencia, described how 'Au(III) on nanocrystalline CeO₂ catalyses the isomerization of α -alkynylfurans to phenols where similar TONs were obtained to those obtained from homogeneous systems.

'Factors affecting activity of gold on hopcalite and other supports' was presented by Jason McPherson of Project AuTEK, South Africa, and its implications for choice of catalysts for use in respirators for protection against CO inhalation during fire escape etc. The improved ambient CO oxidation performance of AuTEK catalysts such as 1wt% Au/TiO₂, especially under high humidity conditions, has been shown to be superior to Au/hopcalite and far superior to hopcalite alone. Collaborative AuTEK/WGC posters entitled 'Progress towards producing stable gold catalysts' and 'Applications for mixed precious metal catalysts containing gold' were presented by David Thompson. Catalysts of increased stability are now being described, and the addition of platinum group metals or silver to gold produces higher activities than for gold itself.

In a poster entitled 'CO oxidation on Au/CeO₂ structured systems' JA Odriozola, CSIC-Universidad de Sevilla, Spain described methods for coating stainless steel, FeCrAlloy and aluminium monoliths with adherent Au/CeO₂. The highest conversion to CO₂ was obtained with the monoliths coated with 1% Au/CeO₂ in the presence of water.

Also in the pollution control section, R Nedvalkova, Institute of Catalysis, Sofia, Bulgaria reported on 'Nano-sized gold-based catalysts for complete benzene oxidation: influence of promoter and support nature on the catalyst's reactivity', and the lowest temperature for 100% conversion (190°C) was achieved over gold-molybdena catalyst supported on ceria. S. Albonetti, University of Bologna, Italy described catalytic combustion of o-dichlorobenzene catalysed by gold-iron promoted with vanadium, on TiO₂.

Results which indicate possibilities for producing durable catalysts were presented by Michael Paul, MPI, Mülheim, Germany, in a talk entitled 'Novel high-temperature stable catalysts by encapsulating Au- and Pt- nanoparticles in MeOx hollow spheres': the hollow shell of mesoporous ZrO₂ or TiO₂ leads to separated catalytically activated particles where treatment at 800°C has no effect on the Au particle size. Veronique Pitchon, CNRS, Strasbourg, France, in her presentation entitled 'How to stabilize gold nanoparticles for high temperature applications?' described the use of fluorites or spinels of formulae Ce₂Zr₂O₈, CeTiO₄ and ZrTiO₄ together with anion exchange using HAuCl₄ as the gold precursor to prepare catalysts stable at 700°C. Rodolfo Zanella, UNAM, Mexico, described Au-Ir/TiO₂ catalysts which are thermally stable for CO oxidation during three reaction cycles.

M Iglesias, CSIC Madrid, presented a talk entitled 'Au vs Pd complexes soluble and heterogenized on MCM-41 as effective and versatile catalysts' where the catalysts are easy to recover and can duplicate the activity of the homogeneous analogues, and no deactivation was observed after repeated recycling.

Aminoalcohols can be converted into aminoacids with high selectivity using gold on oxide catalyst and this route could be used for the production of a range of aminoacids in industry (Alberto Villa, Università di Milano, Italy).

The photoreduction of drinking water nitrates using noble metal catalysts, including gold was described by Jacinto Sa of the University of Aberdeen, UK. Photocatalytic water splitting using Au on semiconductor oxide supports was described by Gian Luca Chiarello of the Università di Milano.

Mechanistic reports

In a talk presented by A Goguet, Queen's University, Belfast, entitled 'Operando quantification of reaction intermediates in the water-gas shift reaction on Au/Ce(La)O₂: elimination of formates seen by DRIFTS as a key intermediate' the conclusions were based on kinetic data obtained at the chemical steady state (3).

In a poster presented by Katia Fajerweg, UPMC, Paris, describing propene oxidation on Au/CeO₂, it was found that reduction of the catalyst in hydrogen led to higher activity, due to the presence of metallic gold. In another poster by Catherine Louis, entitled 'Reducibility of gold(III) precursors: influence of the metal oxide support and consequences for CO oxidation activity' the reducibility of the Au(III) precursor in a CO/O₂/He reaction mixture at 298 K was found to decrease

as a function of the support material in the order titania > ceria > alumina, and the activity obtained for CO oxidation was related to the amount of metallic Au present.

Nina Bogdanchikova, Universidad Nacional Autónoma de México, Ensenada, presented two posters on preparation and properties of gold on zeolite catalysts. The roles of gold clusters, gold nanoparticles and oxidized gold were discussed. A number of kinds of sites can be active in CO oxidation, but Au³⁺ is inactive.

Andreea Gluhoi of Leiden University, The Netherlands in a poster entitled 'What makes Au an intriguing but active catalyst?' reported results which show that the size and shape of the gold particles as well as choice of support and additives and the interaction of the support with the gold all play their part. Alkali (earth) metal oxides influence the stability of Au nanoparticles against sintering by being structural promoters. W. Huang, Hefei, China in a poster entitled 'Anchoring highly active gold nanoparticles on SiO₂ and CoO_x indicated that silica modified with 6% CoO_x prior to loading with gold produces a highly active catalyst for low-temperature CO oxidation by greatly enhancing the dispersion of the gold nanoparticles.

S Rousseau, LCS-CNRS/ENSICAEN, France described methanol oxidation over Au/CeO₂ and Au/TiO₂ catalysts, using operando and in situ FTIR spectroscopy to study the mechanism, including the role of the support and the metal: the formation of methoxy on the support was the rate determining step, and this was followed by its transformation into formate. Maria Ziolk of Mickiewicz University, Poznan, Poland obtained high activity and 100% selectivity for conversion of methanol to formaldehyde using gold on mesoporous silica and metalosilicates. Methanol is oxidized by oxygen strongly held in the mesoporous matrix.

C Milone of the University of Messina, Italy described the 'selective hydrogenation of α,β -unsaturated carbonyl compounds on Au-supported catalysts' where the strong influence of the support suggests that selective sites are those formed by electron transfer from the reduced support to the gold metal particle. For 'Crotonaldehyde hydrogenation on Au/CeO₂ catalysts' Corinne Petit reported a high selectivity to crotyl alcohol (71%) for gold supported on high surface area ceria, and the redox properties of the ceria increased the selectivity of gold to carbonyl hydrogenation.

In 'Origin of selectivity in the gold-catalysed aerobic oxidation of stilbene', Pascal Lignier, CNRS, Lyon, France, tert-butyl hydroperoxide was used together with Au/TiO₂ and other gold catalysts to elucidate the mechanism of the selective (to epoxide) and total oxidation reactions. The role of peroxide is emerging as an important feature of gold-catalysed reactions (4, 5).

Acknowledgements

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References

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