Report on AURICAT Workshop, Gandia, Spain, 11-13 May 2005

As part of the training activities for the postdocs working in our AURICAT EC Network Project, which has research projects on gold catalysis in eight European universities, collaborating with four industrial units and the World Gold Council, this Workshop was efficiently organized by two of the postdocs (Francois Moreau and Silvio Carretin). The current status of gold catalysis was reviewed and the relationships of the AURICAT research work within this topic defined. Some new ideas for applications as well as for new innovative research emerged.

Investigations into gold catalysis are at a very exciting stage. Gold catalysts have been shown to be significantly more active than platinum for carbon monoxide oxidation, and catalyse this oxidation below ambient temperature. Gold also promotes many other reactions when supported on oxides, carbon or polymers or when present as a suitable soluble compound in solution. These reactions include the complete oxidation of hydrocarbons, the water-gas shift, selective oxidation of CO in the presence of hydrogen, oxidation of ethene to vinyl acetate and conversion of ethyne to vinyl chloride, propene to propene oxide, conversion of cyclohexane to cyclohexanone and cyclohexanol, sugars and glycerol to organic acids, ethylene glycol to methyl glycolate, selective hydrogenation of alkynes and dienes in the presence of olefins and aldehyde to alcohol in the presence of an olefinic double bond, incorporation of CO₂ into organic molecules, homogeneous alkyne oxidation and cyclization reactions and hydrogen/oxygen reactions. Gold catalysis is also fascinating because there are interesting examples of gas- and liquid-phase heterogeneous catalysis and homogeneous catalysis in solution. In addition to the high activities recorded for gas phase catalysis, 'naked gold' particles are very active in the liquid phase and very high turnover numbers have been recorded in homogeneous catalysis. There are recent indications that supported gold catalysts are more stable at high temperatures and more poison resistant than was previously thought likely, and this is partly because oxidised gold can play a role in the mechanism as well as nanoparticulate gold(0).

The Workshop opened by the project consultants (David Thompson and Geoffrey Bond) outlining the history of genesis of the EU AURICAT Network Project and the progress made to date with regard to generation of new technology and

publications (40 in the first 2½ years). This high output of publications mirrors the fast growth in gold catalysis publications in general, particularly in the last few years. The principal themes of AURICAT include detailed investigations into preparation methods, including looking at new approaches, mechanisms and model systems, catalyst stability, and novel reactions. The plans for the Workshop were then described. The inputs would take the form of plenary talks and posters and the output would be reports of the resulting discussions which would take place in three groups of parallel sessions with about 10 members in each group. In addition to members of AURICAT some additional academic and industrial participants had been invited to the Workshop and their input to the talks and discussions was greatly valued.

Plenary Presentations

Some of the talks had the following titles and presenters and the timing of these was spread throughout the meeting:

Current status of gold catalysis?

by *Graham Hutchings, University of Cardiff, UK*

Proposed catalytic sites in supported gold catalysts

by *Bruce Gates, University of California, Davis, USA*

Structural and electronic parameters controlling the electronic properties of gold

by *Avelino Corma, ITQ, Valencia, Spain*

Applications for gold catalysis

by *Michele Rossi, University of Milan, Italy*

Activation of molecules on gold-based catalysts

by *Ben Nieuwenhuys, Leiden University, The Netherlands;*

Gold on iron oxides: model studies

by *Shamil Shaikhutdinov, Fritz Haber Institute, Berlin, Germany*

Considerations for a gold catalysed process

by *Larry Ito, Dow Chemical, USA.*

Talks which all took place on the first afternoon/evening consisted of the following:

Au/TiO₂ catalysts prepared by deposition-precipitation

by *Francois Moreau, University of Salford, UK*

Remarkable hydrodechlorination activity over silica-supported nickel-gold catalysts

by *Catherine Louis, UPM Paris*

Effect of preparation techniques on the WGS activity of gold-supported catalyst

by *Donka Andreeva, Institute of Catalysis, Sofia, Bulgaria*

Measure of gold active sites by quantitative chemisorption data and by FTIR

by *Flora Boccuzzi, University of Torino, Italy*

The direct synthesis of hydrogen peroxide using supported Au-Pd catalysts

by *Jennifer Edwards, University of Cardiff, UK*

Large scale synthesis of gold nanoparticles

by *Benedicte Thiebault, Johnson Matthey Technology Centre, UK*

The application of supported gold catalysts for gas phase hydrogenation reactions

by *David Lennon, University of Glasgow, UK*

Heterogeneous catalysts containing Au-free species for homocoupling of aryl boronic acids

by *Silvio Carretin, ITQ, Valencia, Spain*

Gold-catalyzed addition of alcohols to alkynes

by *Kai Gumlich, BASF, Ludwigshafen, Germany*

Liquid phase oxidation using gold based catalyst

by *Nikolaos Dimitratos, University of Milan, Italy*

Use of gold(I) species in homogeneous catalysis of organic molecules including alkynes

by *Carmen Blanco, University of Stuttgart, Germany*

Attributes expected from a gold catalyst

by *Martin Lok and Peter Bishop (Johnson Matthey, Billingham and Reading).*

Poster session

The posters had the following titles:

Gold-vanadia supported catalysts for complete oxidation of hydrocarbons, *Donka Andreeva, Sofia*

Homogeneous Gold(I)-catalysed reactions with alkynes and other functional groups, *Carmen Blanco, Stuttgart*

Spectroscopic features of CO adsorbed on different Au/CeO₂ catalysts, *Flora Boccuzzi, Torino*

Catalytic application of Au-modified catalysts in liquid phase oxidation, *Nikolaos Dimitratos, Milan*

Catalytic application of Au catalysts in gas phase oxidation, *Nikolaos Dimitratos*

Effect of acid washing on the activity of supported Au-Pd catalysts for H₂O₂ synthesis, *Jennifer Edwards, Cardiff*

Asymmetric rhodium-catalyzed hydrogenation meets gold-catalyzed isomerization : the synthesis of chiral, non-racemic 8-hydroxytetrahydroisoquinolines,

Stephen Hashmi, Stuttgart

Gold catalysis: synthesis of dihydroisobenzofuran and isochromane derivatives, *Stephen Hashmi*

Gold catalysis: mild conditions for the synthesis of substituted oxazoles and mechanistic studies, *Stephen Hashmi*

Gold catalysis: synthesis of *o,o,o'*-trisubstituted biaryl compounds, *Stephen Hashmi*

Gold catalysis: mechanistic studies of the phenol synthesis, *Stephen Hashmi*

The preparation of an inherently residue-free alumina-supported gold catalyst and an evaluation of its effectiveness for the hydrogenation of propyne, *David Lennon, Glasgow*

Preparation of supported gold catalysts at the LRS-Paris for various applications, *Catherine Louis, Paris*

Au/TiO₂ with different gold loadings, influence of the pH on the activity for CO oxidation, *Francois Moreau, Salford*
CO adsorption on oxide supported gold nanoparticles, *Shamil Shaithutdinov, Berlin*

Mechanistic studies of water-gas shift reaction with Au supported catalyst, *Bozena Silberova, Delft*

The mechanism of catalysis by gold and its implications for industrial applications, *David Thompson, London*

Workshop sessions

These were organised around three topics and the following aspects were discussed in each of three parallel sessions. The overall objectives were to review the field of gold catalysis, to identify problems and major areas for growth, to achieve a better understanding of previous work and to identify new techniques (theoretical or experimental) needed to make further progress in research in the field of gold catalysis and its application.

Topic A: Reaction Mechanisms

Session 1: chemisorption on gold surfaces and catalysts (especially oxygen, hydrogen, etc): participation of support sites, use of lattice oxygen: mechanism of selective oxidations

Session 2: mechanism of CO oxidation, PROX and water-gas shift: DFT calculations

Session 3: mechanisms of other reactions of industrial / environmental importance (H₂O₂ synthesis, selective hydrogenation, NO_x reduction, etc)

Topic B: Catalyst Structure

Session 1: dependence of structure on method of preparation, especially supported and model catalysts;

similarities and differences between single crystals, 'models' and 'real' catalysts: techniques for characterisation

Session 2: the oxidation state of gold, *in situ* and *ex-situ* techniques: use of EXAFS, XANES: theoretical input : bimetallic catalysts

Session 3: stability of gold catalysts, poisoning, sintering; reactivation: deterioration on storage, causes and prevention

Topic C: Reactions and Applications

Session 1: trends in current research; keeping up with the literature: the most promising avenues to explore: identifying the unique features of gold that should define future openings for its use

Session 2: preparing the way for major industrial chemical manufacturing processes, including selective oxidation and hydrogenation: large-scale manufacture of catalysts and their recovery: identifying where gold might be used most advantageously

Session 3: environmental applications : in vehicle exhaust, air purification, fuel cells, sensors, NO_x abatement, etc

The plenary talks and posters were all well presented and the discussion documents written beforehand by the session leaders also helped to stimulate lively discussion. The outcome of the various discussions was presented by each session leader in a plenary closing meeting and these outputs will be analysed and integrated into a final report before deciding on appropriate actions and relevant further investigations. It is already clear, however, that the AURICAT team is making significant contributions to our understanding of gold catalysis and its further development into useful applications, and both these aspects will be assisted by the outcome of this Workshop which proved to be a successful and very worthwhile exercise.

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