

Conference Report

Gold Catalysis Highlights at 20NAM, Houston, Texas, USA, 17–22 June 2007

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A short report on the significance of gold catalysis within this stimulating conference is included in the *CatGold News* section of this issue. Of the many oral and poster presentations the following highlighted the potential of gold catalysts for commercial applications (see www.20nam.org) and new developments in thinking on mechanisms. The new results from aqueous phase oxidation reactions described by Robert Davis were particularly noteworthy.

Papers with potential for commercial applications

Opportunities for water pollution control were indicated in a talk by Michael Wong, Rice University, Houston entitled 'Prospects for reductive catalysis in groundwater remediation: bimetallic nanoparticles for water-phase hydrodechlorination': catalyst activity is dramatically increased using Au-Pd nanoparticles rather than Pd for the trichloroethene to ethane reaction. In a poster presentation the resistance of Au-Pd nanoparticles to sulfur and chloride poisoning was described by Kimberley Heck from the same group. Another paper on hydrodechlorination was presented by Catherine Louis, of Université Pierre et Marie Curie, Paris, this time using Au-Ni catalysts for chloroarenes such as 1,2-dichlorophenol and entitled 'Silica and titania-supported Ni-Au catalyst: application in hydrodechlorination'.

There was plenty of evidence of gaseous pollution control opportunities using gold catalysis for removing pollutants from living spaces, and in purifying hydrogen. 'Commercial applications of gold catalysts for CO oxidation – performance, deactivation and regeneration, was presented by Jason McPherson, Project AuTEK, S Africa, where applications in respirators, air-conditioning and hydrogen purification for use in fuel cells on vehicles (AuroPureH₂) are foreseen, especially once acceptable service life will meet specifications. There were a number of other presentations on CO oxidation (see below) and PROX (preferential removal of CO from hydrogen). The current position on durability for gold catalysts was

summarized in a WGC/Project AuTEK poster entitled 'A review of progress towards producing stable gold catalysts by CW Corti, RJ Holliday, E van der Lingen and DT Thompson. Very high durability, selectivity and yield have already been demonstrated for the oxidation of glucose to gluconic acid in the liquid phase where specific activities and conversions remain steady for 110 days (N Thielecke, U Prüsse and K-D Vorlop, *Catal Today*, 2007, **122**, 266).

'New routes to key commodity chemicals' were discussed by Claus Christensen, Technical University of Denmark, Lyngby, with reference to the conversion of bioethanol to acetic acid in 90% conversion and 80% selectivity using Au/TiO₂ or Au/MgAl₂O₄. This route provides a green alternative to acetic acid obtained from methanol and fossil feedstock sources. The kinetics of propene oxidation over gold-titania catalysts were described by Alexander Nijhuis of Eindhoven University, The Netherlands: this provided insight into how to improve the hydrogen efficiency by reducing water production. Ronald Mentz et al, BASF Catalysts Beachwood, Ohio, described the next generation of Au-Pd catalysts for the production of vinyl acetate from ethene, acetic acid and oxygen: improved activity and selectivity has been achieved at equal metal loading.

Selective hydrogenation has until recently been a rather neglected area of catalysis by gold, but it has important applications potential for removing alkadienes and alkynes from the olefin streams used for polymer production. In a paper entitled 'Gold-based catalyst performance in selective hydrogenation of butadiene in an excess of propene', Antoine Hugon, Laurent Delannoy and Catherine Louis (UPMC, Paris) showed that gold catalysts are much more selective than Pd, partly because they are less active, but within a large window of temperatures, the conversion of butadiene is 100% and the selectivity to alkenes is close to 100%. Another paper on selective hydrogenation, by Yolanda Segura, Núria López and Javez Pérez-Ramirez was entitled 'Origin of the superior selectivity of gold particles for hydrogenation of triple bonds in alkyne-alkene mixtures': selectivities of 85 – 95% were achieved for the hydrogenation of propyne in propene mixtures over a Au/CeO₂ catalyst.

The cyclotrimerization of acetylene to benzene using Au-Pd surfaces was reported by KK Gath, D Kumar, T Wei, M Chen and DW Goodman (Texas A&M University). At all compositions studied an Au/Pd surface is more active than a pure Pd surface for acetylene trimerization to benzene. This enhanced activity is attributed to the formation of isolated Pd sites, ie a Pd atom surrounded by Au atoms. Benzene is used in the manufacture of dyes, explosives, detergents and pharmaceuticals.

Greater mechanistic understanding

'Nanoengineering supports for gold catalysts via selective surface functionalization' by Sheng Dai, Haoguo Zhu, Wenfu Yan and Steven H Overbury' (Oak Ridge National Laboratory,

TN) described work on layer-by-layer functionalization techniques to create complex support surfaces with 3D-structures containing oxide cavities for the immobilization of gold nanoparticles, preventing sintering and increasing durability. From another Oak Ridge presentation it was concluded that for Au nanoparticles on silica and titania weak CO adsorption and low CO coverages under reaction conditions suggest that the availability of CO may vary sensitively with particle shape changes. In a paper entitled 'Design and synthesis of highly active supported Au catalysts', MS Chen, Z Yan, F Yang and D W Goodman, Texas A&M University, have shown that a continuous Au bilayer film is very active for CO oxidation. In the presentation 'CO oxidation on nanotowers formed from Au/CeO₂ multilayers, Zheng Zou, Howard Salsburg and Maria Flytzani-Stephanopoulos, Tufts University, Medford, MA, USA it was stated that the interfacial length of Au and CeO₂ layers can be correlated with CO reaction rate. Juan Henao et al of Northwestern University, Evanston, IL, in collaboration with Jeffrey Miller of BP, Naperville, showed that bromide suppresses the activity for CO oxidation by a different mechanism on an unactivated (oxidized) from an activated (reduced) Au/TiO₂, and the results are consistent with the active sites being metallic Au. Low temperature CO oxidation kinetics for dendrimer templated supported Au catalysts is being studied by Bert Chandler et al (Trinity University, San Antonio); and the synthesis of mono- and bi-metallic nanoparticle catalysts using dendrimers was reported in other presentations by this research group.

Gabriel Veith of Oak Ridge National Laboratory, TN, described his use of physical vapour deposition via magnetron sputtering to prepare gold catalysts on unusual supports such as boron oxide, nitride and carbide and the mechanistic insights they provide for CO oxidation. In a poster entitled 'Understanding the effect of halide poisoning in CO oxidation over TiO₂', Zhen Ma et al of Oak Ridge have studied the use of phosphate supports for CO oxidation and found that the resulting Au/LaPO₄ catalysts are very active.

Papers reporting the mild conditions under which water-gas shift takes place in the presence of gold catalysts were given by Robbie Burch of Queen's University, UK ('In situ characterization of catalytic systems: differentiating actors and spectators for the water-gas shift (WGS) reaction on Pt and Au catalysts') where formates were demonstrated not to be important intermediates using in situ infrared spectroscopy, and Chan Hwan Kim of University of Michigan ('Mobility of surface species on supported water gas shift catalysts: isotopic exchange of ¹⁸O₂ with ¹⁶O of CeO₂ and CeO₂-ZrO₂') which provided insight into the deactivation mechanism. Christopher Hardacre of Queen's University also described a mechanistic study of the water-gas shift and identified where improvements are necessary if long-life catalysts are to be obtained. Mechanistic and deactivation studies on water-gas shift were also reported by Michiel Makkee, Delft University of Technology, The Netherlands.

In a poster entitled 'Nanostructured Au/CeO₂ and Au/Fe₂O₃ catalysts for the CO oxidation and water-gas shift reactions',

W Deng, M Flytzani-Stephanopoulos, F Boccuzzi and M Manzoli, Tufts University, Medford, MA and University of Turin, Italy, found that the WGS activation energy (49±7 kJ/mol) is the same for both these catalysts and suggest that this points to activation of -OH from the oxide support playing a part in the mechanism. In a paper from Brookhaven National Laboratory, Upton, New York, P Liu and JA Rodriguez suggest that large catalytic activity of Au/CeO₂ in the water-gas shift reaction is based on the fact that CeO₂ is directly involved in lowering the water dissociation barrier and substantially facilitating the reaction. Sergio Gomez (Mexico) presented evidence interpreted as indicating the presence of both Au nanoparticles and gold cationic species in Au/CeO₂ catalyst during PROX.

Amongst the plenary lectures was one by Prof RJ Davis of the University of Virginia, Charlottesville in which he described work on the use of Au/C and unsupported Au powder at high pH to catalyse the oxidation of glycerol and CO in the liquid (aqueous) phase. For oxidation of CO in water at pH 14 and 300 K, the turnover frequency (TOF) for 5 nm Au particles was 5 s⁻¹, whereas the TOF for large supported Au (42 nm) and bulk Au were 0.5 and 0.4 s⁻¹ respectively, and the observed rate of peroxide formation during CO oxidation was also much higher on the small Au particles. In the oxidation of glycerol using 5nm Au particles a TOF of 17 s⁻¹ was obtained at pH 13.8; larger Au particles being less active but more selective for formation of glyceric acid. This work indicates the importance of determining the roles of peroxide and alkaline conditions in the mechanisms of gold catalysed oxidation reactions in water.

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