Faraday Discussion 152: ‘Gold’

Geoffrey Bond

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Abstract Faraday Discussion 152 on ‘Gold’ was held at the University of Cardiff from 4th to 6th July 2011 with about 80 participants; the 21 papers read and discussed reflect current themes in gold catalysis.

Keywords Catalysis · Gold

Faraday Discussions are probably unique among scientific conferences in that contributions accepted by the organisers on the basis of abstracts submitted some 9 months before the meeting have then to be processed into full texts that are also vetted; if approved, these are then circulated to participants a few weeks in advance of the meeting, at which one of the authors is allowed only 5 min to present a summary of the work. An extended and searching period of open discussion then follows. It is generally accepted that Faraday Discussions often set the tone for the next phase of research in the subject.

The meeting started with a wide-ranging lecture entitled ‘Perimeter Interfaces in Catalysis’ by M. Haruta (Tokyo Metropolitan University), who has been largely responsible for the rapid growth of interest in gold’s catalytic properties; this was not pre-printed, so its publication is eagerly awaited.

Anyone hoping to hear of exciting new developments in gold catalysis with the prospect of practical application will however have been disappointed. A great deal of emphasis was placed on the use of theoretical methods, particularly density functional theory (DFT) and on the study of ‘model’ systems, i.e. on reactions conducted in an ultrahigh vacuum

(UHV) apparatus and having questionable relevance to useful catalysis. With only one or two exceptions there was little interest in reaction mechanisms or in the use of kinetic methods to suggest them; not a single new activation energy or order of reaction was reported.

Structural studies

Thin gold films formed by physical vapour deposition onto a titanium layer overlaying an indium tin oxide glass showed electrocatalytic activity that was apparently associated with defect sites (Plowman, O’Mullane and Bhargava, RMIT University, Australia). Aberration-corrected analytical electron microscopy applied to palladium–gold colloids attached to either carbon or titania supports revealed structural information that was related to catalytic performance in benzyl alcohol oxidation and H₂O₂ synthesis (Titvalam, Pritchard, Dimitratos, Lopez-Sanchez, Edwards, Carley, Hutchings and Kiely, Cardiff University and Lehigh University, Bethlehem PA); unfortunately, none of the materials studied had outstandingly good catalytic properties. ‘Nanoporous’ gold formed by dissolving silver from an Au–Ag alloy was found to catalyse CO and methanol oxidation (Wittstock, Wichmann, Biener and Bäumer, University of Bremen); residual silver had a marked positive effect on catalytic performance. Detailed structural work on gold islands formed on ruthenium supported by graphene has been conducted; they conform to the corrugation of the underlying grapheme (Xu, Semidey-Flecha, Liu, Zhou and Goodman, Oak Ridge National Laboratory, TN and Texas A&M University).

G. Bond (✉)
9 Townfield,
Rickmansworth WD3 7DD, UK
e-mail: geoffrey10bond@aol.com

Theoretical advances

DFT calculations of O₂ chemisorption on Au/Fe₃O₄ showed that it occurred at the metal–support interface, the gold atoms involved becoming substantially oxidised (Howard and Willock, Cardiff University). Auophilic attractions between a closed-shell gold cluster and a closed-shell Au^I molecule were examined theoretically (Pyykkö, Xiong and Li, Helsinki University and Tsinghua University, China), and fundamental steps in homogeneous gold catalysis (activation by coordination, protodeauration and transmetalation from gold to palladium) were also analysed by DFT methodology (Hashmi, Pernpointner and Hansmann, Heidelberg University). Corner and edge atoms were identified as the location for the dissociative chemisorption of H₂ on gold nanoparticles (Lyalin and Taketsugu, Hokkaido University, Japan).

Model studies using UHV systems

There is a deep-seated belief that studies of ‘model’ systems by surface science methods, that is, using single crystal gold surfaces, produce information that illuminates the behaviour of nanoparticles in ‘real’ systems. Thus, for example the exothermic reaction of O₂ with the Au–H bond on Au(111) was proposed as a route for O₂ chemisorption in gold-catalysed oxidations (Campbell, Sharp, Yao, Karp and Silbaugh, University of Washington), although it is not obvious where the H atoms originate, except possibly from the chemisorption of water. The rate of CO oxidation as a function of the size of particles formed by vapour deposition onto TiO₂(110) showed that it varied as the -2.4 power of their diameter, again suggesting a predominant role for low-coordinated sites (Saint-Lager, Laoufi, Bailly, Robach and Dollo, Université Joseph Fourier and Institut Nanosciences et Cryogénie, Grenoble). Two papers emanating from Harvard University sought to demonstrate that gold-catalysed oxidations could be explored by using the Au(111) surface on which O atoms had been set down by decomposing ozone. The first paper reported on the O-assisted amine–aldehyde coupling, the desorption of the product amide being rate-controlling (Xu, Friend and Madix); the second dealt with the oxidative coupling of alcohols and showed that the ease of beta-H elimination determined product distributions (Xu and Friend).

Gold clusters

Small gold clusters (e.g. $N=13$) in the presence of Co and O₂ were shown to be significantly fluxional by parallel

tempering and atomistic thermodynamics (Beret, Ghiringelli and Scheffler, Fritz Haber Institute, Berlin); this raises the question of whether structural models based on static particles are helpful in understanding how CO oxidation works. The gaseous cluster dimer Au₂⁺ is able to dehydrogenate methane to ethane (Lang and Bernhardt, University of Ulm, Germany).

Kinetic methods

Although not popular as a method of study, three papers relating to their use caused animated discussion. The mechanism of the water–gas shift on supported gold catalysts has been much discussed; the de Donder relations were employed to derive rate expressions, and these, supplemented by DFT calculations, led to a complex mechanistic scheme for the reaction (Chen, Wang, Burch, Hardacre and Hu, Queens University, Belfast). A kinetic study of propene oxidation showed that propene oxide formation was most dependent on the H₂ concentration, an active peroxo species (Au–OOH) being required (Chen, Halin, Schouten and Nijhuis, Eindhoven University of Technology). Attempts to derive a precise description of the electronic structure of very small (<3 nm) gold particles, combined with re-analysis of published results, led to the conclusion that their high activity for CO oxidation depended on their being in a non-metallic molecular state (Bond, Brunel University).

Selective oxidation

Gold, both supported and unsupported, is well known for its ability to catalyse the selective oxidation of polyhydroxylic compounds such as glycerol to hydroxy acids. With either carbon nanotubes or nanofibres as supports, this reaction depends much on the basic character of the support induced by oxidation followed by treatment with NH₃ (Prati, Villa, Chan-Thaw, Arrigo, Wang and Su, Università degli Studi, Milan, Fritz Haber Institute, Berlin, and Institut für Nanotechnologie, Karlsruhe, Germany). The conversion of allyl alcohol (propenol) to 3-hydroxypropionic acid is a more complex reaction, involving first the hydration of the C=C bond, then the oxidation of C–OH to –COOH; it is catalysed by Au/C catalysts, particularly well when 1% of copper or platinum is also present (Falletta, Pina, Rossi, He, Kiely and Hutchings, Università degli Studi, Milan, Lehigh University, and University of Cardiff). Metallic gold particles are removed from supported catalysts by dissolution in NaCN solution, but those that are left (~0.1% in the case of Au/SiO₂) remain active for the oxidation of benzyl alcohol (Thomas, He and Edwards, University of Cardiff); they are presumably very small and non-metallic.

Miscellaneous

Gold nanoparticle–polymer or –biopolymer complexes appear to have an important future for protein sensing (Moyano, Rana, Bunz and Rotello, University of Massachusetts and Georgia Institute of Technology, USA). There were also two lively poster sessions, where 33 displays of published and unpublished work were presented for discussion. The Conference Banquet was addressed by

the President of the Faraday Division of the Royal Society of Chemistry; he recalled former Discussions on catalysis and expressed the belief that number 152 was a worthy successor to them.

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