Gold: A Relatively New Catalyst*

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Work performed with gold catalysts before about 1980 is briefly reviewed, and early indications of the importance of using very small particles to obtain good activity are noted. The apparent contrast between silver and gold in catalysing carbon monoxide oxidation was anticipated by studies in matrix isolation chemistry. The unexpected and in some ways unique properties of gold are attributable to the operation of a relativistic effect which stabilises the $6s^2$ electron pair. Essential requirements for high oxidation activity include: small particle size, use of 'reactive' support, and a preparative method that achieves the desired size of particle in intimate contact with the support. Surface atoms on such small particles behave more like individual atoms, and this together with awareness of the relativistic factor may help to explain why gold can be such an effective catalyst.

Attendance at the conference entitled 'Catalytic Gold 2001' held in Cape Town in April 2001 bore witness to the dramatic growth of interest in the catalytic power of gold that has occurred over the past 15 years. This is very largely due to the pioneering work of Dr M. Haruta, which has stimulated research in many other centres, and has brought gold catalysis to the verge of significant application. Although there has been sporadic interest in the subject throughout the 20th Century, none of this earlier work gave any promise of useful activity, and in view of the great advances in other areas of catalyst technology, including the development of very important catalytic processes based on copper and silver, one is entitled to ask what has caused the delay. The short answer is, and many papers in the Conference confirmed this, that gold catalysis is a very special kind of animal, only manifesting itself under quite specific circumstances: realising this, it is not so surprising that its arrival was delayed for so long. In this sense gold is a relatively *new* catalyst.

It was long believed that gold failed as a catalyst because its power of chemisorption was far too small and that the superior performance of the Platinum Group Metals for many reactions was due to their stronger chemisorption tendency. It was in fact only to be expected that gold should fail on this count. The Tanaka-Tamaru Rule (1) had shown that initial enthalpies of chemisorption of oxygen and other molecules are linearly related to the enthalpies of formation of the most stable oxides. This implies that chemisorbed oxygen atoms are energetically similar to atoms or ions in bulk oxides, and the nobility of gold, which is due to the instability of its oxide Au_2O_3 (ΔH_f = +19.3 kJ mol^{-1}), also determines its inability to chemisorb oxygen in the bulk state.

THE UNUSUAL PROPERTIES OF GOLD

The absence of a stable oxide is unique to gold: for all other elements, including silver, their oxides have negative free energies of formation. There are many other respects in which the properties of gold, compared to those of its neighbours, are unexpected (2, 3). Its metallic radius is slightly smaller than that of silver (see Figure 1 for selected physical properties of gold and its neighbours), but the Au^{III} state is more stable than Au^{I}, while the reverse is true for silver. Gold has a high electronegativity for a metal, as shown by its high first ionisation potential, and it can form compounds such as Au^-Cs^+ where it is anionic. These and many other unusual characteristics are reflected in the chemistry of mercury, which has a quite unusual crystal structure and a melting temperature below ambient.

The differences between the 4*d* and 5*d* elements and their compounds have been ascribed to the great stability of the $6s^2$ electron pair. This is now thought to originate in an operation of Einstein's Theory of Special Relativity on the energies of electron orbits (3 - 6). The theory can only be outlined here in the following very short summary. As the mass of the nucleus increases, the innermost 1*s* electrons have to increase their speed to maintain their position, and for gold they attain a speed which is about 60% that of light. There is then a relativistic effect on their mass, and the 1*s* orbital contracts: all the outer *s* orbitals have to contract in sympathy, but *p* and *d* electrons are

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* This paper was given as the opening keynote lecture at the 'Catalytic Gold 2001' Conference held in Cape Town, April 2001.

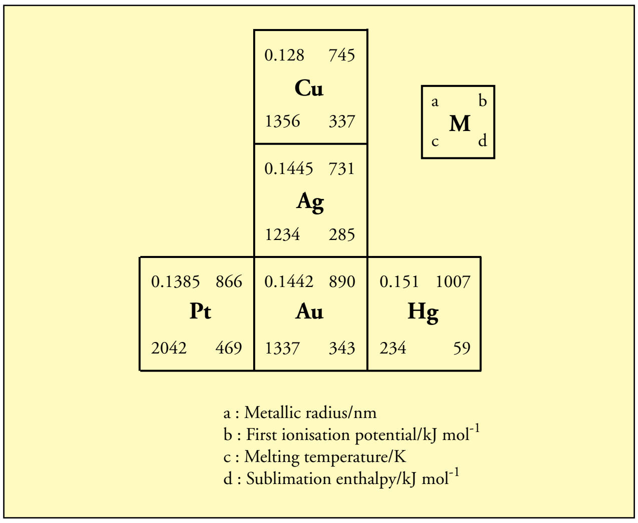

Figure 1 *Some physical properties of platinum, mercury and the metals of Group 11: clockwise from top left, metallic radius/nm; first ionisation potential/kJ mol^{-1}; melting temperature/K; and sublimation enthalpy/kJ mol^{-1}*

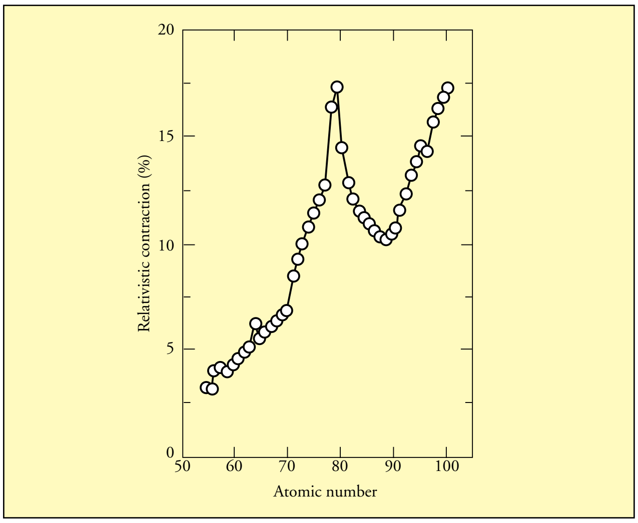

Figure 2 *Calculated relativistic contraction of the 6s level as a function of atomic number Z. The actual size of the 6s electron shell for Pt and Au is some 15% smaller than it would be in the absence of the relativistic effect*

much less affected. In consequence the $6s^2$ pair is contracted and stabilised (Figure 2), and much of the chemistry (including the catalytic properties (4, 5)) of the $5d$ elements is determined by the high energy and reactivity of the $5d$ electrons.

Although this idea is very helpful in understanding why gold differs so much from its neighbours, it only rationalises the view held until recently that gold was almost useless as a catalyst. Clearly something is missing from our analysis.

A VERY SHORT HISTORY OF GOLD CATALYSIS

The belief that "There is no new thing under the sun" is as valid for the history of science as elsewhere: everything has its antecedents, and the explosion of interest in gold catalysis in recent years was preceded by years of endeavour to which due regard should be paid. The oxidation of hydrogen on a gold gauze was observed as early as 1906 (6), in what must have been one of the first attempts to assess the dependence of rate in a gas-phase reaction upon reactant pressures: subsequent studies (7, 8) confirmed and extended these results. The earliest reference to gold as a catalyst for carbon monoxide oxidation dates from 1925 (9). A slow trickle of papers appeared through the 1950s and 60s, and these were reviewed in 1971 (10): this paper referred to work (11) in which gold reportedly acted as a *hydrogenation* catalyst, utilising hydrogen atoms that had surprisingly diffused through a gold film from a palladium–silver diffusion thimble. A further significant contribution was made by Professor G. J. Hutchings and his associates, who realised that the very high standard electrode potential of gold (+1.4V) would make $AuCl_3$ a very effective catalyst for the hydrochlorination of ethyne: and so it proved (12).

During the 1970s there were two areas of work which anticipated the developments to come. In the first (2, 13, 14) it was shown that gold supported on alumina and especially on silica was active for alkene hydrogenation at 373K. With silica as support, good activities were shown by catalysts having only very low gold contents (0.01 – 0.05%), these showing the typical colour of colloidal gold (13), with turnover frequencies 7000 times greater than shown by higher loadings, and also failing to show the double-bond isomerisation usually seen with other metals.

The second prophetic study (15, 16) was in the field of matrix isolation chemistry, in which metal atoms and simple molecules are co-condensed with a rare gas to form a solid at extremely low temperature: on raising the temperature, complexes of low stability may be formed, and studied for example by spectroscopic techniques. This procedure was exploited by G. A. Ozin in Toronto and produced much exciting new chemistry which has been largely ignored. Its relevance to catalysis is that these unstable complexes may resemble those that are transient intermediates in catalysed reactions at higher temperatures. McIntosh and Ozin (16) examined the reactions of silver and of gold atoms with oxygen: silver formed the colourless $Ag^+(O_2)$ while gold formed a green $Au(O_2)$ molecule in which the oxygen molecule bonded sideways on, as if it were an alkene. On reacting with carbon monoxide, the reactions shown in Figure 3 occurred, and it was suggested that what happened with gold might be a model for the mechanism of the heterogeneously- catalysed oxidation.

This short survey serves to show that gold is only a *relatively* new catalyst.

SMALL GOLD PARTICLES

These last two pieces of research lead us naturally to identify the origins of the very high activities now possible with supported gold catalysts, and one connecting theme is the requirement for gold particles not larger than about 4nm (2). As the size of a metal particle is decreased, a number of things happen: (i) obviously the fraction of surface atoms increases, and because these vibrate more freely the melting temperature falls and surface atom mobility rises. (ii) Because the overlap of electron orbitals decreases as the average number of bonds between atoms becomes less, the band structure is weakened, and surface atoms in particular start to behave more as individuals than as members of the club. (iii) At the same time, a greater fraction of the atoms comes into contact with the support, and the length of the periphery per unit mass of metals rises.

These three factors, plus the operation of the relativistic factor, may serve to explain why carbon monoxide is more strongly chemisorbed on gold than on silver, but this has not yet been exposed to rigorous theoretical analysis (see however (17)). There is indeed another well-established requirement for high activity: this is the presence of a support for the small gold particles from which oxygen ions can be extracted to give surface anion vacancies on which oxygen molecules can adsorb as superoxide ions (O_2^-)(18). These then attack carbon monoxide molecules chemisorbed on the gold particles, possibly after they have reacted with a support hydroxyl group to make a formate ion $(HCOO^-)$. This mechanism, first suggested by Iwasawa (19), bears a close resemblance to that proposed by Ozin (15, 16) for the reaction catalysed by unstable gold complexes (Figure 3). The final need is for a preparative method to secure the necessary small particle size in intimate contact with the support.

The fine details of reaction mechanism may differ from one catalyst to another, and much remains to be done to elucidate them (17). The literature on bifunctional and spillover catalysis may provide some inspiration.

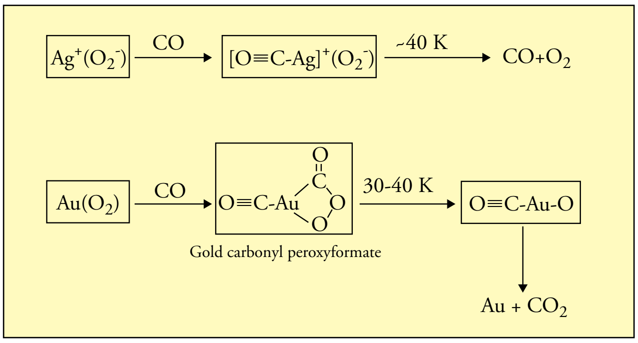

Figure 3 *Reactions of silver and gold oxygen complexes with carbon monoxide in a solid inert gas matrix (15, 16).*

THE FUTURE

It is worth noting that the use of 'reactive' transition metal oxides such as Fe_2O_3, NiO and MnO_2 that have proved so beneficial to the oxidation activity of gold catalysts has not yet been applied to other metals such as platinum and silver: nor have the methods of coprecipitation and deposition-precipitation been used on the 4*d* metals, for which they would certainly work. Conversely the extensive work on Ag/Al_2O_3 catalysts for oxidation of ethene to oxirane has not yet been applied to gold. Although we are well past the beginning of the discovery of gold's catalytic potential, the best may be yet to come, and a golden future lies ahead.

ABOUT THE AUTHOR

Geoffrey Bond held academic posts at Leeds and Hull Universities before joining Johnson Matthey plc in 1962 as Head of Catalysis Research. In 1970 he was appointed Professor in Brunel University's Chemistry Department, and is now an Emeritus Professor: he has 'Visiting' appointments at the Universities of Salford and Surrey.

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