

An overview of gold-catalysed oxidation processes

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Gold and gold/platinum group metals (Au/PGM) catalysts are active under mild conditions or even at ambient temperature or less and this makes them unique. They will therefore be effective in reducing running costs of chemical plants and increasing the selectivity of the reactions involved where applicable. In pollution control applications such as air cleaning, low light-off autocatalysts, and purification of hydrogen streams used for fuel cells they have the characteristics to become the catalysts of choice, especially now that their durability and resistance to poisons is being shown to be better than was anticipated. The mechanisms of these gold catalysed reactions are still uncertain but both oxidised and metallic gold are probably involved, and the details depend on types of reaction and the conditions used.

KEY WORDS: gold; gold/platinum group metals; chemical processing; pollution control; fuel cells.

1. Introduction

Gold supported on oxides or carbon is now firmly established as an effective gas phase oxidation catalyst under mild conditions [1–3] and examples of reactions catalysed include carbon monoxide oxidation, and complete and selective oxidation of hydrocarbons and other organic materials. Consideration of the water gas shift reaction (WGS) in which hydrogen is produced from water via the simultaneous oxidation of carbon monoxide to carbon dioxide is also considered. Current developments in liquid phase homogeneous and heterogeneous catalysis will be highlighted. These include the use of supported gold catalysts for the oxidation of glucose to gluconic acid [4], an important food and beverage additive, and the selective oxidation of other sugars [5]. Homogeneous catalysis by gold complexes involves both novel syntheses and/or high turnover numbers [6]. These results in solution and the liquid phase indicate that gold has intrinsic catalytic activity when liganded or metallic as well as when oxidised or promoted by oxides.

2. Practical developments

The reaction which received most initial publicity regarding catalysis by gold was the complete oxidation of CO to CO₂ which takes place under very mild (<room temperature) conditions [7,8] (figure 1).

Since this impressive pioneering work, a very large number of papers has been published on CO oxidation and the variables affecting activity and mechanism studied in depth. For example, Moreau et al., have

shown that use of high pH reduces chloride levels; and small gold particles are best for activity [9] (table 1). It is not necessary to calcine the catalysts.

Early speculative attempts to explain the mechanism of CO oxidation using gold catalysts invoked involvement of both Au⁰ and oxidised gold [10] and chemisorption of CO onto Au metal and movement of an hydroxyl ion from the support to an Au(III) ion (figure 2).

Figure 2 is a representation of the early stages of the oxidation of carbon monoxide at the periphery of an active gold particle. At the left, a carbon monoxide molecule is chemisorbed onto a low coordination number gold atom, and an hydroxyl ion has moved from the support to an Au^{III} ion, creating an anion vacancy. At the right they have reacted to form a carboxylate group, and an oxygen molecule occupies the anion vacancy as O₂⁻. This then oxidizes the carboxylate group by abstracting a hydrogen atom, forming carbon dioxide, and the resulting hydroperoxide ion HO₂⁻ then oxidizes a further carboxylate species forming another carbon dioxide and restoring two hydroxyl ions to the support surface. This completes the catalytic cycle. No attempt was made to suggest the charges carried by the reacting species. As yet, there is no experimental evidence as to whether the oxygen derives from the gas or the support, and details of the mechanism may vary depending on choice of oxide support and reaction conditions.

Recently SIMS spectra of Au/ γ -Al₂O₃ and Au/TiO₂ catalysts provided evidence for the presence of the oxidised Au clusters AuO⁻, AuOH⁻ and AuO₂⁻ and this is consistent with the active site being an ensemble of Au-OH and metallic Au [11].

Durability is a feature about which doubts have been expressed for gold catalysts, since the melting point of gold (1337 K) is much less than that for platinum

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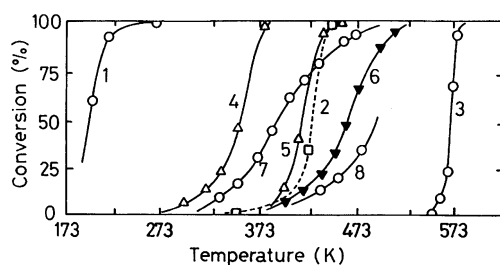


Figure 1. Oxidation efficiencies for carbon monoxide oxidation for Au/ α -Fe₂O₃ in relation to catalyst temperature in comparison with other catalysts. 1 Au/ α -Fe₂O₃ (Au/Fe = 1:19), prepared by co-precipitation; 2 0.5 wt% Pd/ γ -Al₂O₃, prepared by impregnation; 3 gold fine powder; 4 Co₃O₄, ex-carbonate; 5 NiO; 6 α -Fe₂O₃; 7 5wt% Au/ α -Fe₂O₃, prepared by impregnation; 8 5wt% Au/ γ -Al₂O₃, prepared by impregnation. (Based on reference [8]).

Table 1
Specific rates for CO oxidation for Au/TiO₂ catalysts [9]

Au wt%	Temp (K)	10 ⁴ mol CO s ⁻¹ g Au ⁻¹	Final pH in preparation
0.5	300	7.3	8.6–9.0 ^a
0.5	300	0.76	7–10
0.06–1.9	300	61	9 ^b

^aUnder mass transport control.

^bUnder kinetic control.

(2042 K) particles would sinter at around 500 °C (i. e. its Tamman temperature). There are, however, firm indications of stability at temperatures higher than this. Using a two-stage impregnation procedure, involving removal of residual chloride with base, Datye and co workers [12] found that the gold particles were hydrothermally stable in 10% H₂O at 600 °C for 100 h. The addition of transition metal oxides to form for example Au/MnO_x/MgO/Al₂O₃ catalysts has been found to suppress Au particle sintering in methane oxidation up to 740 °C [13]. The formation of ionic gold trapped in an oxide lattice is thought to be responsible for the stability of some Toyota catalysts: there was no

reduction in T_{50%} conversion for propene after treatment at 800 °C for 5 h (table 2). A standard Au/Al₂O₃ catalyst under the same conditions suffered significant degradation.

During investigations aimed at reducing CO levels in hydrogen feeds for fuel cells, we have studied a range of Au-based catalysts and find that Au/CeO₂-ZrO₂ catalysts are highly active for the water gas shift reaction (WGS) and produce hydrogen from water at as low a temperature as 100 °C. Characterisation of these catalysts indicates that they contain gold in an ionic form and it is ionic rather than metallic gold which is responsible for the high activity of these catalysts. Kinetic studies of the reaction show that it is positive order in CO and H₂O but negative order in CO₂ and H₂ and that the reaction mechanism may be significantly different from that for a Pt/CeO₂ catalyst [15]. In figure 3 the activities for a commercial copper catalyst are compared with that for gold and platinum catalysts and the advantages for the gold catalysts at low temperatures can be clearly seen. The fact that the Au/CeO₂-ZrO₂ catalysts show 20% CO conversion at 100 °C is particularly noteworthy.

Consistent with ionic gold playing a significant role in the WGS are the results obtained by Flytzani-Stephanopoulos and co workers [16]. These workers leached away the metallic gold with cyanide from Au/CeO₂ catalysts until the gold content was only at 0.2–0.9% Au and the catalyst was free of metallic gold particles. The activity of the resulting catalysts was similar to that of the unleached catalysts and it was concluded that ionic gold was the active species.

In a recent Chevron patent [17] it is claimed that a gold catalyst may be used for both high- and low-temperature water gas shift reactions. 0.1–3.0 wt% Au/sulfated ZrO₂ (0.02–2.5 wt% sulfur) were used and for example, 98.2% conversion was obtained at 20,000 GHSV over 350 h at 200 °C and 30 psig.

This patent provides evidence of advantages for the presence of sulfur in catalysis by gold. This is interesting

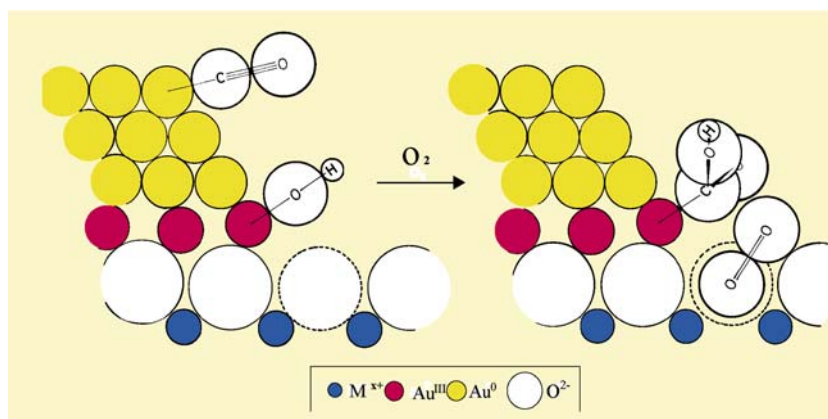


Figure 2. Representation of a possible mechanism for the oxidation of carbon monoxide using gold on an oxide support [10].

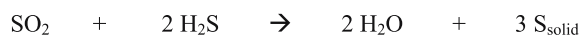
Table 2
Catalyst for purifying an exhaust gas (Toyota) [14]

Catalyst composition		Temp. at 50% C ₃ H ₆ conversion (°C) ^a	
Chemical Formula	Au content (wt%)	Initial	After durability test ^b
Au ₂ Sr ₅ O ₈	0.4	345	346
Au ₂ Sr ₅ O ₈	0.4	340	355
La ₂ Au _{0.5} Li _{0.5} O ₄	0.2	341	348
La ₂ Au _{0.5} Li _{0.5} O ₄	0.2	344	345
Au/Al ₂ O ₃	2	378	433

^aEvaluation conditions: CO 1000 ppm, C₃H₆ 670 ppm C, NO 250 ppm, O₂ 7.3%, H₂ 5%, balance N₂ at 150,000 h⁻¹.

^bDurability test conditions: CO 1000 ppm, C₃H₆ 670 ppm C, NO 500 ppm, O₂ 6.5%, CO₂ 10%, H₂O 10, %, balance N₂ at gas temperature of 800°C for 5 h.

because another area of doubt in using gold catalysts was thought to be that of potential poisoning. Further evidence of resistance to sulfur poisoning is provided by the results of Lui *et al.* (Brookhaven National Laboratory, USA) [18]. He found that Au/TiO₂ is 5–10 times more active than pure titania for the reduction of SO₂ by CO and also 5–10 times more active for the Claus reaction:

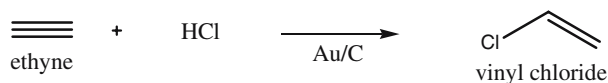


Hydrodesulfurisation reactions are also catalysed by gold [19] and it has been demonstrated that for dibenzothiophene the conversion increases by a factor of 6 when going from pure Pd to 1:1 Au:Pd and pure gold is even more active than the pure palladium catalyst. Such enhanced activity was explained in terms of the well known affinity of gold for sulfur which activates the

breakage of the C–S bond without forming stable inactive sulfur species.

The use of gold catalyst in the WGS may obviate the need for further purification of hydrogen streams using the PROX reaction, but the use of gold catalysts before the hydrogen stream enters the fuel cell may be used to reduce the CO impurity since gold is more selective for the CO to CO₂ reaction than for the H₂ to H₂O reaction and removal of the CO prevents poisoning of the Pt fuel cell catalyst [20]. The presence of sodium in the gold catalyst decreases the TOF for Au/Fe₂O₃ and should therefore be thoroughly removed by washing [21]. Au/ZrO₂ obtained from Au_{0.5}Zr_{0.5} alloy gives good selectivity for oxidation of CO in the presence of H₂ in the 50–70 °C range [22], but gold catalysts can also perform the PROX reaction efficiently at ambient temperatures [20].

The conversion of ethyne to vinyl chloride using an Au/C catalyst was a very early significant breakthrough in catalysis by gold:



The potential advantage of using gold rather than mercury for this reaction was predicted by Hutchings in 1985 [23] who proposed that the activity of metal chlorides could be correlated with the electron affinity of the cation, i.e. that the standard electrode potential should be a more suitable parameter for the correlation of catalytic activity: any metal cation with a higher electrode potential than Hg²⁺ would be expected to give enhanced catalytic activity. On this basis gold cations should to be the most active catalysts for this reaction. This was subsequently confirmed experimentally and

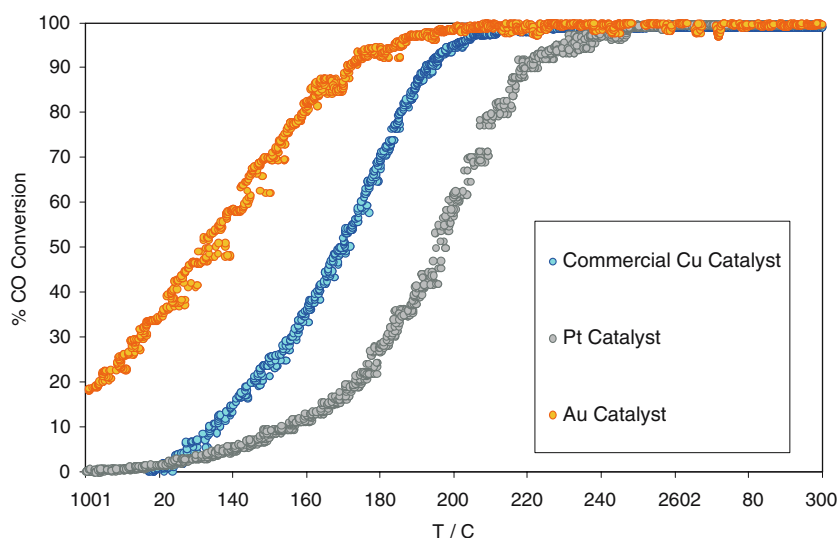


Figure 3. Comparison between activities of copper, platinum and gold catalysts in the water gas shift reaction (MHSV = 40,000 cm³ g⁻¹ h⁻¹) [15].

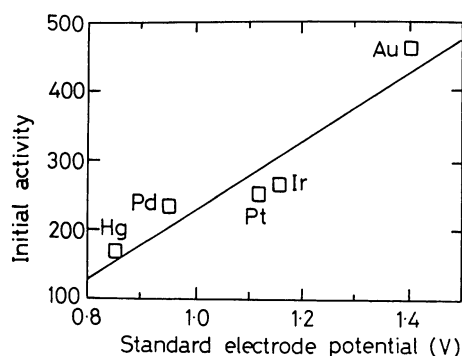
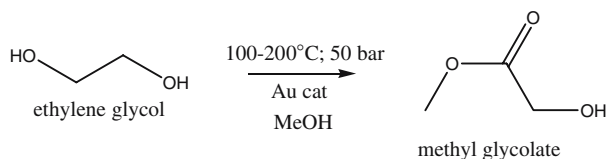


Figure 4. Correlation of initial hydrochlorination activity (mol HCl mol metal⁻¹ h⁻¹) of metal chlorides supported on carbon (453 K, GHSV 1140 h⁻¹) with standard electrode potential: catalysts contained 5×10^{-4} mol metal/100 g catalyst [24].

gold catalysts were found to be about 3 times more active than the commercial mercuric chloride catalysts used at that time [24,25] (figure 4).

Vinyl chloride is the important intermediate needed for the manufacture of polyvinyl chloride (PVC). However, 1 tonne of gold would be needed for each plant and this was thought to be too expensive in the 1980s when the price of gold was around 3 times its present value: at today's gold price, the use of gold in this conversion would surely be viable, especially when the recovery and recycle of the gold is taken into account.

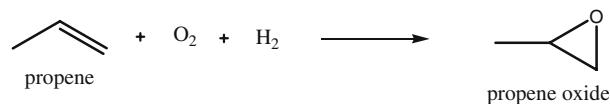
Nippon Shokubai has developed a gold-based catalyst that enables the methyl ester of glycolic acid to be made directly from ethylene glycol [26]:



A 50 M tonne per annum pilot plant has been commissioned and there are plans to build a larger scale plant in about 3 years time. The proprietary catalyst is a nano-sized dispersion of activated gold supported on a metal oxide carrier such as Au/TiO₂-SiO₂, used in the presence of oxygen and the conditions indicated in the above reaction scheme. Methyl glycolate can be used as a solvent for semiconductor manufacturing processes, as a building block for cosmetics and as a cleaner for boilers and metals. The Nippon Shokubai announcement also indicates that the catalyst technology will be used for other syntheses involving one-step esterification of carboxylic acids and lactones. One of their patents claims its use for the synthesis of methyl methacrylate.

One of the selective oxidation reactions which has attracted intense attention because of its industrial importance is the epoxidation of propene. Current commercial production of propene oxide (PO), used

extensively in the production of polyurethanes, is often based on a chlorohydrin process. However, the direct gas-phase synthesis of PO from propene using molecular oxygen in the presence of hydrogen, offers the opportunity to eliminate chlorine from the production process, as well as reduce water consumption and salt by-products:



Patents for direct propene oxide production using gold catalysts have been appearing in the literature [27-29], indicating significant industrial interest in this application, and pilot plants are understood to be operating within the industry. Bayer researchers have claimed an 8% yield of propene oxide [28], with 95% selectivity.

Haruta [30] obtained >99% selectivities at low conversions in the oxidation of propene to propene oxide using a 1 wt% Au/TiO₂ catalyst system at 50 °C, when both oxygen and hydrogen are present in the feed gas (H₂:O₂: propene: Ar = 10:10:10:70 vol%). More recently published work has improved these results further, such that yields are at a commercially acceptable level [31]. At 13 ICC in Paris (July 2004) [32], Masatake Haruta reported PO yields of 9% when using a silylation treatment and alkaline earth metal salts as promoters. Table 3 summarizes some of the results from a recent paper [33].

It was concluded that nanoparticle-support interaction is required together with careful selection of the TiO-SiO support material and control of the Au-particle size. The use of pH 7.0 in the DP method was also recommended, together with calcination at 300 °C. Results from a Dow patent are given in table 4: they closely parallel those reported by Haruta.

The remaining technical challenge is the need to increase catalyst durability further, with deactivation currently occurring after a few hours on stream.

The potential of gold as an important catalyst in chemical processing is thus clearly established. An

Table 3
Selectivities and yields for propene (pp) epoxidation using titanasilicate supported catalysts prepared by a modified sol gel method [33]

Au %	PP Conv	H ₂ Conv	PO Sel	PO yield
0.42	3.4%	35%	85.4%	4.0%
0.6	4.5	32.1	79.6	5.6
0.007	1.0	3.5	100	1.0

TiO-SiO support, Space Velocity 4000 h⁻¹ cm³/gcat, feed Ar/C₃H₆/H₂/O₂ = 70/10/10/10, Temperature 150 °C, Ti/Si = 2/100; prepared by sol-gel method. Catalysts calcined at 300 °C.

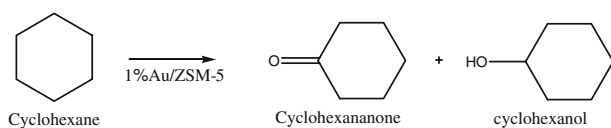
Table 4
Propene (pp) propene oxide (po), reported by Dow [34]

T °C	PP Conv mole %	PO sel mole %	H ₂ O/PO mole ratio	g PO per kg cat h
160	0.36	92	2.04/1	8.3

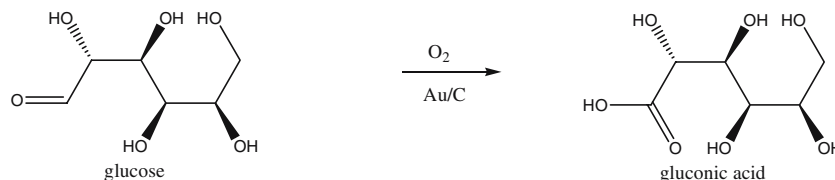
Feed stream: 20% propene, 10% H₂, 10% O₂, + He

2 g cat, flow rate 160 cm³ min⁻¹, olefin GHSV, 480 h⁻¹, atm pressure
Catalyst 0.5 wt% TiO-SiO: calcined at 550 °C.

important recent development is the demonstration [35] that gold catalysts can be used in a solventless liquid phase system to oxidize cyclohexane to cyclohexanone and cyclohexanol using oxygen. Almost all the cyclohexane produced (4.4 million tonnes per annum, and expected to grow at ca 3%) is converted to cyclohexanone and cyclohexanol, the intermediates in the production of caprolactam and adipic acid used in the manufacture of nylon-6 and nylon-66 polymers. The present commercial process for cyclohexane oxidation is carried out at around 150 °C and 1–2 MPa with ca 4% conversion and 70–85% selectivity to cyclohexanone and cyclohexanol. The large demand for these products and the high energy demands for the present process could provide an opening for a more effective catalyst. Comparatively high conversion rates of ca 15% and high selectivities to cyclohexanone and cyclohexanol with TONs of up to ca 3,000 h⁻¹ can now be achieved, using 1% Au/ZSM-5 catalysts:



in addition, the reaction occurs in an environmentally benign oxidation protocol involving oxygen as the oxi-

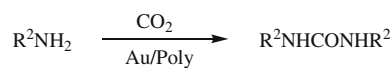


dant in a solvent-free system. The catalyst also seems durable at least within the limits tried so far. A Solutia Inc. USA patent describing similar technology was published in August 2004 [36].

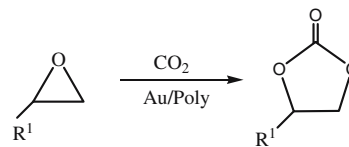
A remarkable paper has been published describing the activation of CO₂ with a polymer-supported gold catalyst to give substituted ureas and acid anhydrides [37].

The activation of carbon dioxide and the TOFs obtained are really noteworthy (table 5).

The high liquid phase activity for 'naked' gold sols compared with similar preparations of other precious



R² = benzyl, chlorohexyl



R¹ = CH₃-, (CH₃)₂CHOCH₂-, PhOCH₂- and ClCH₂

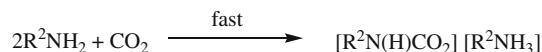


Table 5
Epoxypropane reaction with CO₂ over Au/polymer [37]

Catalyst	GC yield	TOF/h
0.1 wt% Au/polymer	53	57,900
0.05	71.2	15,400

Reaction conditions: 30 atm CO₂, 150 °C, 5 h

metals has been demonstrated by Biella and Rossi [4] (figure 5). The activity of gold observed for the first 200 s corresponds to a mean TOF value of 11340 h⁻¹ mol gluconic acid per mol Au.

In order to increase the life of the 'naked' colloidal gold, however, it is necessary to support it on carbon. Gold-on-carbon catalysts can be used very effectively to oxidize glucose to gluconic acid (an important food additive and cleansing agent, made on the 60,000 tonnes per annum scale) [4]:

It is pertinent to evaluate whether there could be further opportunities for gold in the food industry: if so, this may have the appeal that any gold residues in the products could be completely harmless since gold is thought to be environmentally benign as it has no known toxic effects.

At the 13 ICC in Paris, new results were presented relating to gold-catalysed sugar chemistry. The first by Mirescu *et al.* [5] reported on the selective oxidation of lactose and maltose with Au/TiO₂ catalysts, which was used to give 100% selectivity to lactobionic acid and maltobionic acid respectively:

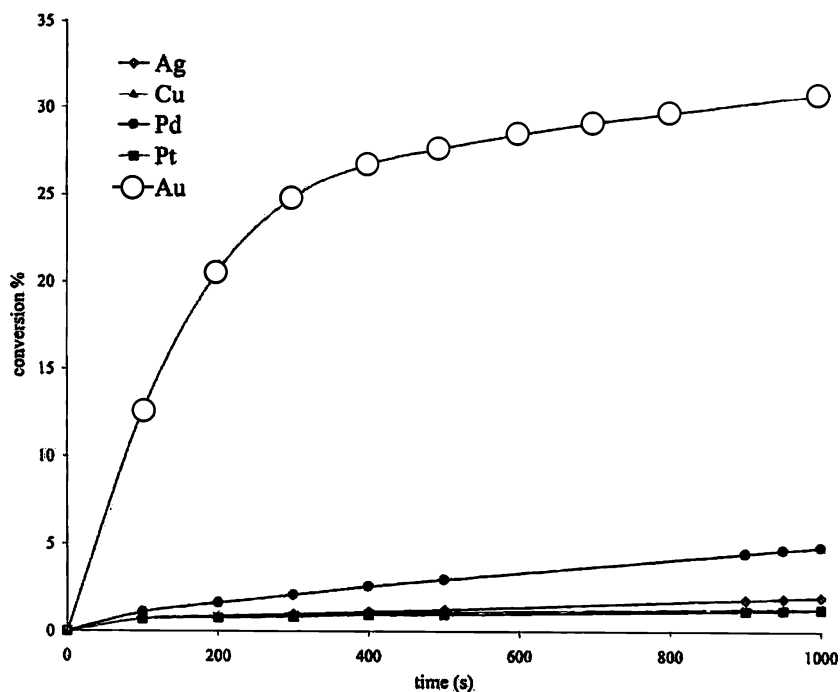
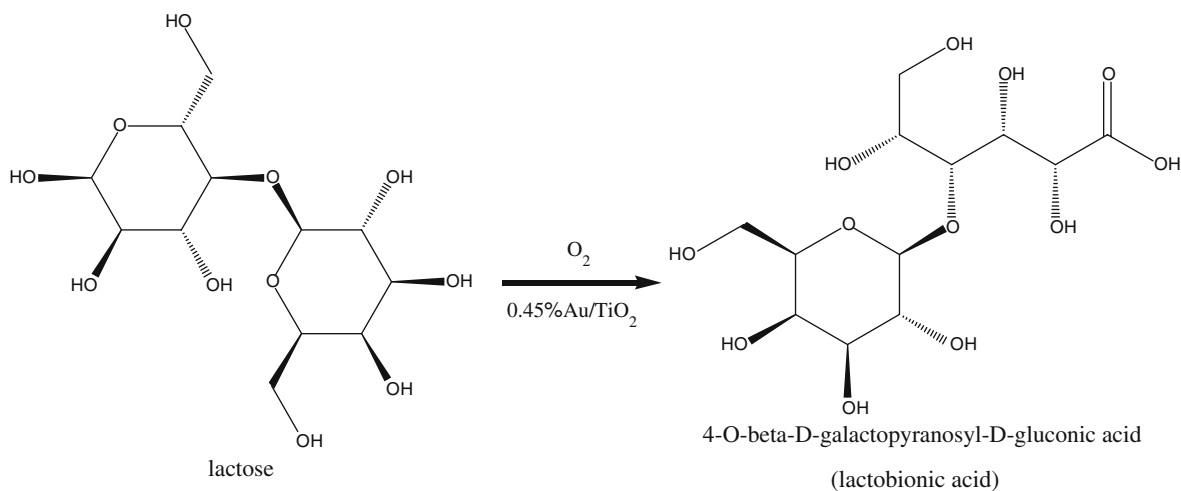
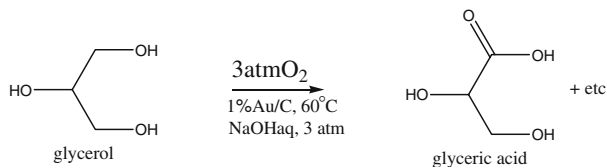


Figure 5. Comparative activities for 'naked' colloidal gold and other metal sols in the oxidation of glucose to gluconic acid [4].

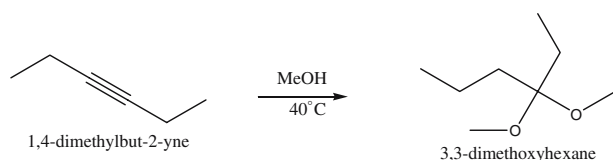


The initial activity for maltose was more than twice that for lactose but both reactions gave 100% selectivity to maltobionic acid and lactobionic acid respectively. The two acids have potential uses in the pharmaceutical and detergent industries. Additional results were reported by Claus and co workers who studied the catalytic conversion of glucose under hydrogenation and oxidation conditions to produce sorbitol and gluconic acid respectively [38].

The oxidation of glycerol to glyceric acid with 100% selectivity using either 1% Au/charcoal or 1% Au/graphite has been reported to take place under mild conditions: ca 55% conversion was obtained in 3 h at 60 °C [39]:



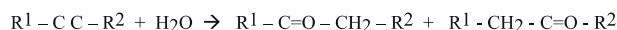
The status for homogeneous catalysis by gold in solution has been dramatically transformed by the results of Teles and coworkers [40]. This BASF group have described the use of cationic gold (I) complexes of the type [L-Au⁺] (where L is a phosphane, phosphite or an arsine) for the addition of alcohols to alkynes. An example of such a reaction is given in Equation:



the turnover numbers for this type of reaction are up to 2×10^5 moles of product per mole of catalyst, with turnover frequencies of up to 5400 h^{-1} . These gold catalyst systems are a significant improvement on the mercury catalysts used previously and the reactions are conducted under mild conditions (293–323 K) in the presence of acid co-catalysts.

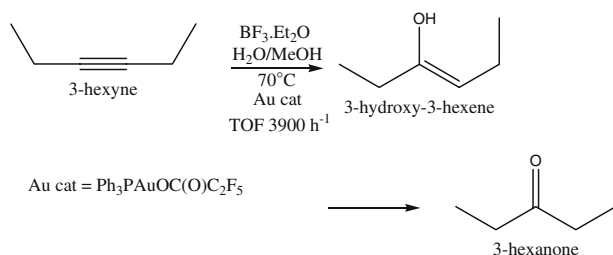
This breakthrough has now been followed by the work of Stephen Hashmi and coworkers at the University of Stuttgart [41] where it has been shown that soluble gold species can be used to catalyse the formation of new carbon-oxygen and carbon-carbon bonds. A recently reported example is given in figure 6.

With as little as 0.07 mole% of AuCl_3 pyridine catalyst a complete conversion could be achieved: this corresponds to a TON for this reaction of 1180 [42]. Hayashi and co workers [43,44] have studied the use of $(\text{Ph}_3\text{P})\text{AuCH}_3$ and acid co-catalysts for the hydration of alkynes to give ketones:



Turnover numbers in the range 3,500–15,600 h^{-1} were reported.

Schmidbaur and co workers [45] have reported high turnover frequencies for the addition of water to an acetylenic triple bond:



In the past, the involvement of gold complexes of any type in homogeneous catalysis has been very rare: this is in marked contrast to those for the platinum group metals, many of which readily undergo catalytic oxidative-addition/reductive-elimination cycles. This has been

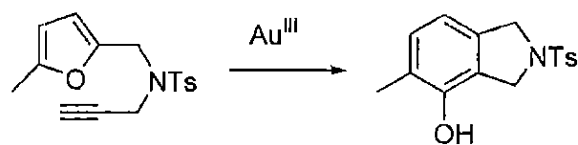


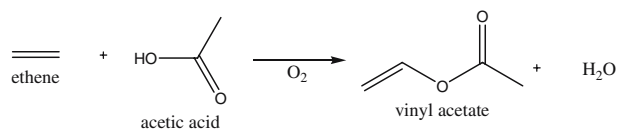
Figure 6. An example of a cyclisation reaction with a homogeneous gold catalyst ($\text{AuCl}_3 \cdot \text{py}$) which has a TON of 1180 [40].

rationalised by saying that this type of catalysis requires a very delicate balance between the stabilities of the two oxidation states involved, and this has not often been achieved for gold. An additional factor was thought to be the reluctance of gold to form hydride complexes, so that the oxidation of gold(I) by dihydrogen, or the formation of alkene complexes by β -elimination in gold(III)-alkyl complexes is virtually unknown. For other precious metals, the relative stabilities of the two critical oxidation states has been successfully adjusted by appropriate choice of ligands, e.g. the inclusion of a good π -bonding ligand, such as carbonyl, increases the stability of the lower oxidation state. With gold, π -bonding has seemed to be of relatively little importance. This kind of thinking was supported experimentally to the extent that the few examples of homogeneous catalysis by gold reported in the literature were associated with very small turnover frequencies and yields of product per mole of catalyst. New thinking is, however, now required to rationalize the dramatic increases in TONs and TOFs recently reported by Teles, Hashmi, Hayashi and others: the mechanisms could have unique features.

3. Mixed Au/PGM catalysts

The recent surge of new interest in catalysis by gold nanoparticles [31,46,47] has now led researchers to investigate the effects of the addition of other metals to the gold [48]. As a result, there are a number of reactions with potential for industrial application where combinations of gold with a platinum group metal (PGM) have been shown to have advantages over either gold or the PGM alone. A number of reactions that benefit from the synergy of a PGM with gold are now described.

It is interesting to reflect that vinyl acetate monomer (VAM) has been produced industrially for some time from acetic acid, ethene and oxygen using palladium-gold (Pd-Au) catalysts in a fixed bed process. The reaction proceeds with selectivities as high as 95% [49]:



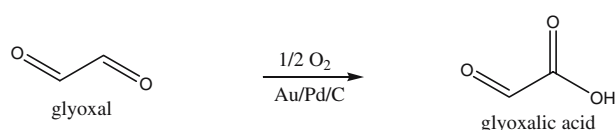
Work at Dupont by Provine *et al.* [49] utilising Pd-Au silica-supported catalysts promoted with potassium acetate showed that the addition of gold to palladium can significantly improve the rate of production for VAM, see table 6. The first fluidised bed process for VAM has now been commissioned by BP, for a new plant in Hull, U.K. [50]. This process, has been developed by BP Chemicals as a more cost effective route, and allows process simplification and intensification.

Table 6
Yields of vinyl acetate monomer as reported by Dupont [49]

Catalyst	VAM space time yield, g/l h)	VAM selectivity, %
Au/Pd/KOAc	764	93.6
Pd/KOAc	100	95.4
Au/Pd	594	91.6
Pd	124	94.7

Compared with the two reactors usually needed in the fixed bed process, the fluidised process requires only a single reactor. A new catalyst was required for the fluidised operation, and the VAM catalyst that was selected is a Au/Pd mix developed in collaboration with Johnson Matthey; in the form of spheres so fine that they almost appear to flow as a liquid. Thus, a nanocatalyst of Au/PGM is finding use on an industrial scale in this process. Vinyl acetate is used in the manufacture of emulsion-based paints, wallpaper paste and wood glue.

For the synthesis of glyoxalic acid from glyoxal, it has been shown that an Au/Pd/C catalyst is twice as active as Pd/C for this reaction [51]:



Studies by Prati and co workers [52] have shown that the activity for the oxidation of glycerol to glyceric acid is higher for Au/PGM/C (PGM = Pd, Pt) than for Au/C (table 7) (see also above for work using Au/C, reported by Hutchings and coworkers [39]).

Mixed Au-PGM/C activity enhancement compared with the activities found for monometallic catalysts has also been observed in the selective oxidation of D-sorbitol to gluconic and gulonic acids [53]. The Au-Pd and Au-Pt catalysts are poison resistant compared with single element Pd and Pt catalysts.

A mixed metal effect in the hydrodesulfurisation of benzothiophene has already been mentioned when discussing poison resistance of gold and Au-Pd catalysts (see above).

There is a need for the hydrogen peroxide to be synthesised where it is to be used to avoid the heavy transport costs of this hazardous material [54]. Hydrogen peroxide has many uses in chemicals manufacture and can be used as a bleaching agent/disinfectant. Both

Table 7
Mixed metal catalytic effects for the oxidation of glycerol to glyceric acid [52]

1%Au-M/C	TOF h ⁻¹
Au	1090
Au-Pd	1775
Au-Pt	1953

theoretical calculations [55] and experimental results have shown that the formation of H₂O₂ from hydrogen and oxygen is favoured over gold surfaces. Hutchings and coworkers [54] have shown that H₂O₂ can be formed at a high rate with a supported gold catalyst, with selectivity for H₂O₂ over a Au/Al₂O₃ catalyst of 53%. This supported Au catalyst produced more H₂O₂ than the supported Pd catalyst used to date in industry. However, more interestingly, a supported Au/Pd (1:1 wt) catalyst produces even more H₂O₂ than the pure Au catalyst. This indicates there is a synergistic effect by Pd acting as a promoter for the Au catalyst. Furthermore, they showed that the metal nanoparticles are in fact Au/Pd alloys (table 8).

However, it is perhaps in the area of fuel cells that the biggest potential for using Au/PGM catalysts may lie. Zhong and coworkers [56,57] have prepared Au/Pt/C nanoparticle electrocatalysts using a two-phase protocol and these can be used to catalyse the hydrogen/oxygen reaction to produce water in the fuel cell.

The potential advantages of using gold in fuel cells are that Au is cheaper than Pt (ca. 50%) and Au is a good conductor; Au in an Au/Pt alloy will reduce the CO poisoning effect on Pt and there is a decreasing tendency for Pt-OH formation. A method for synthesising gold-platinum bimetallic nanoparticles in aqueous media has been devised via one-phase reduction of AuCl₄⁻ and PtCl₄²⁻ using a combination of reducing and capping agents: hydrogen served as the reducing agent for Pt(II) and acrylate for the reduction of Au(III) [57]. This enabled the preparation of AuPt bimetallic particles with bimetallic compositions in the range 4–90% Au and particle sizes from 2 to 8 nm. It was necessary to devise this innovative approach since bulk bimetallic AuPt metals have a miscibility gap over a wide composition range.

Au and Au-Pt catalysts have been evaluated for the oxygen reduction reaction at the fuel cell cathode [56]. The electrochemical results obtained to date indicate that the bimetallic Au-Pt catalysts have significantly different electrocatalytic properties than either Au or Pt alone. The catalytic activity of Au-Pt is highly dependent on composition and calcination history. Work is continuing on optimising the properties of these cata-

Table 8
Formation of H₂O₂ from the reaction between H₂ and O₂ over Au and Pd catalysts in methanol under 3.7 MPa Pressure (adapted from reference [54])

Catalyst	Temperature (K)	O ₂ /H ₂ mol ratio	H ₂ O ₂ ^a (mmol/g _{cat} h ⁻¹)
Au/Al ₂ O ₃	275	1.2	1530
Au:Pd (1:1)/Al ₂ O ₃	275	1.2	4460
Pd/Al ₂ O ₃	275	1.2	370

^aRate of H₂O₂ averaged over 30 min experiment.

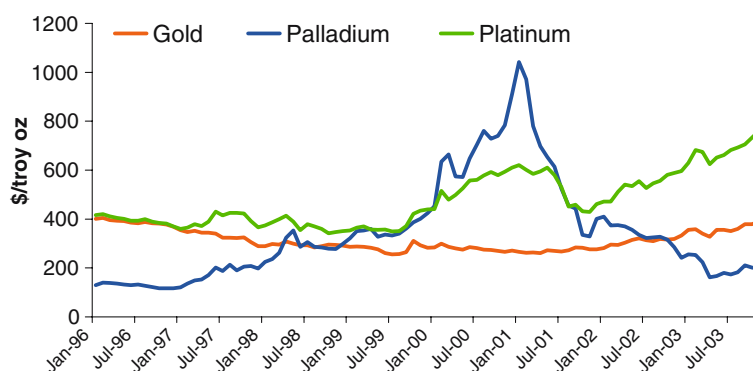


Figure 7. Precious metals prices 1996–2004 [27].

lysts for use in both acid and alkaline fuel cells. Sintering is being limited by removal of chloride.

4. Availability of gold

The most important motivating factor for new catalyst development from a chemical company's point of view is often selectivity. Catalyst cost is not as significant an issue compared to the operating efficiency of a multi million dollar plant. In essence, the intrinsic value of precious metal catalysts is less important than their cost effectiveness and precious metals are economically recycled [27].

Catalyst cost and availability is, however an issue in some significant applications such as fuel cells. It is relevant therefore to compare the prices of the precious metals. Since gold is mined in far greater quantities than platinum or palladium, its price has historically been more stable, figure 7, than these metals and industrialists prefer stable prices. In addition, there is also an improved recognition that gold is not expensive compared to platinum. Due to the considerably greater availability of gold, any significant new demand for gold as a catalyst is unlikely to impact on gold price to any significant extent, unlike the PGMs where demand can outstrip supply with a consequent impact on price, as seen in recent years for palladium. This is an important economic factor in the choice of technology, particularly in emerging industries such as the fuel cell industry.

5. Conclusions

The results described in this review, as summarised in Table 9, demonstrate the intrinsic capability of gold and gold/PGM alloys to be really active catalysts! Not only can gold be a good catalyst when supported on oxides and carbon, and its complexes active homogeneously, it is very active in its colloidal state ('naked' gold), and when supported on polymers. A variety of substantial commercial applications will gradually emerge from the exciting results reviewed in this paper, and developments from these.

Table 9
Examples of reactions catalysed by gold and/or gold/PGMs

Reaction	Quoted references
Oxidation of CO	[1–3,7–11]
Oxidation of hydrocarbons	[1,2,13,14]
Water gas shift	[15–17]
Selective oxidation of CO in hydrogen ('PROX')	[20–22]
Ethyne to vinyl chloride	[23–25]
Ethene to vinyl acetate	[49,50]
Ethylene glycol to methyl glycolate	[26]
Propene to propene oxide	[28–34]
Cyclohexane to cyclohexanone and cyclohexanol	[35,36]
Sugars and glycerol to organic acids	[4,5,38,52,53]
CO ₂ activation	[37]
Homogeneous alkyne oxidation	[40,43,44]
Homogeneous C–O and C–C bond formation	[41,42]
Direct hydrogen peroxide synthesis	[54,55]
Reaction of hydrogen with oxygen in a fuel cell	[56–58]

The commercial potential for gold catalysts has recently been reviewed [27] and includes applications in emission control technologies, chemical processing in a number of bulk and specialty chemical processes, and the emerging hydrogen economy for clean hydrogen production and fuel cell systems. Sensors to detect poisonous and flammable gases or substances in solution are also being developed based on gold. Industrial interest in increased use of gold catalysts is indicated by the steady flow of new patents in many of the applications described above.

In addition to applications already described others could include the decomposition of ozone when generated in living areas, the oxidation of ethene to remove it from food storage containers, and the removal of CO and other gases from living atmospheres. Use in automotive diesel exhausts is also a possibility, as it is in conjunction with three way catalysts (TWC) to overcome a cold start-up problem [59].

Recent research has suggested that gold-based catalysts could be effectively employed in hydrogen processing and related fuel cell systems. Three possible areas have been identified where gold catalysts could be

advantageously applied in fuel cell hydrogen supply systems and in the fuel cell itself [60]:

- Water gas shift (WGS) for clean H₂ production
- Oxidative selective removal of CO from H₂ feedstocks or within the fuel cell membrane (including PROX and AuroPure H₂)
- The use of gold or gold alloys as an electrocatalyst within the fuel cell itself

The fact that gold catalysts operate under very mild conditions makes them unique, with potential for uses not able to be met by other catalysts, but their development is still in the early stages for most applications and more studies on how to make them more stable and more durable are currently underway.

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