

# Progress towards the commercial application of gold catalysts

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Now that gold catalysis is a valuable and exciting new field of catalysis as a whole, the exploitation of gold catalysts for commercial applications is being pursued. This is being assisted by new work on preparation and utilization methods to increase their durability during use. Other factors, including a substantial increase in investment in gold catalysis R&D, need to be considered before widespread application will occur. We show that new opportunities for commercial exploitation can be monitored via patent mapping, followed by careful examination of key patents.

**KEY WORDS:** gold catalysts; durability; patent mapping; patent analysis; commercial applications.

## 1. Introduction

Gold catalysis as a scientific discipline can be said to have come of age. It is now some 20 years since the initial breakthroughs of Hutchings and Haruta [1–5] showed that gold can be an excellent catalyst, in contrast to the existing perception that it was unlike other precious and transition metals in terms of catalytic activity. As demonstrated at the recent GOLD 2006 international conference, subtitled ‘New industrial applications for gold’, held in Limerick, Ireland in September 2006, gold can catalyse an increasingly large number of commercially important reactions and in many instances it performs well against competitor catalyst materials. At GOLD 2006, there were over 60 oral and almost 100 poster presentations on aspects of gold catalysis [6]. The credentials of gold catalysts as part of the ‘Green Chemistry’ movement were also underlined by Hutchings at the conference [7].

As a catalyst, gold is unique [8, 9] and there are examples of chemical transformations as yet not accomplished by any other metals. The ability of gold to catalyse reactions at ambient or sub-ambient temperatures opens up totally new application opportunities. In fact, this ability to catalyse reactions at low temperatures creates an entirely new field of low temperature catalysis with characteristics not previously encountered [7, 10]. For example, deactivation at room temperature is not due to sintering. When catalysts are operated at higher temperatures, any impurity formation can be burnt off. This does not occur at ambient temperatures but solutions to this problem are available. For example, Au/TiO<sub>2</sub> catalysts for cleaning living atmospheres at ambient temperatures can be regenerated by photoirradiation and the poisoning of gold catalysts via carbonate deposition by interaction of the support with atmospheric CO<sub>2</sub> can be avoided by storing the catalyst in a

closed canister at room temperature. The catalyst can keep its activity under these conditions for 2 years [7, 11].

Significant progress has been made since we last reviewed the potential of gold catalysts for commercial applications [12–15] and in this review we summarize the principal recent advances. These include catalysis of a number of additional reactions and demonstration of stability in the liquid and gas phase for use in the following fields of application:

- Pollution and emission control and safety systems
- Hydrogen economy/fuel cell systems
- Speciality/bulk chemical synthesis

As applications for gold catalysts are developed, commercially available sources of catalysts become increasingly important. It is therefore encouraging that Project AuTEK in South Africa has already made 20 kg quantities of gold catalysts and 3 M, Johnson Matthey, Degussa and Sud Chemie all have the capability of manufacturing gold and gold alloy catalysts (see below). The price of gold will be important but the extensive use in commercial catalysis of other precious metals such as palladium, platinum and rhodium suggest that gold will be employed when its catalysts meet selectivity and activity targets. Gold catalysts are particularly active at low temperatures and in this and some other characteristics are unique and therefore may sometimes be the only option for a particular application.

Gold catalysis is now at that stage of development where it is moving into the exploitation phase [7]. This is demonstrated by the increasing number of patents being taken by industrial companies, many of which are household names, as well as R & D organisations seeking to commercialise their intellectual property. A problem here is to be able to follow the commercial trends and identify promising areas of technology where commercial opportunities can be

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realised. Patent mapping is a powerful tool in this respect [16, 17].

World Gold Council has an active programme to promote exploitation of new gold science and technology, as discussed elsewhere [18]. Gold catalysis is at the forefront of this activity and we anticipate new industrial applications to be commercialised in the next 2–5 years. However, the successful introduction of new commercial applications depends on a number of factors, both technical and economic. In this paper, we explore progress towards commercialisation of applications involving gold catalysts, particularly from a patent perspective, and start from a review of patent activity via the patent mapping approach. From this, we focus on promising reactions that we consider have strong commercial prospects and where patent activity is evident in the context of advancing exploitation. Some of the factors necessary to see successful commercial realization, including increased levels of investment in appropriate R&D, will also be discussed.

## 2. Commercial intelligence: patents

Patents can be a very useful source of technical and commercial intelligence and can be used to identify current themes within almost any field of industrial research. For example, advanced software has recently been used to identify patents relating to osmium, a platinum group metal, and to visualise the search results in a patent landscape [16]. The landscapes were created using the Aureka ThemeScape™ [19] software which uses statistical algorithms to analyse the usage of certain words and phrases, and then construct themes and groupings among documents.

In recent work, we have undertaken comprehensive patent searches on the keywords ‘gold’ and ‘catalyst’ covering the period 1996 to 2005 in the US, EP, PCT, GB and JP patent collections. Figure 1 shows a ThemeScape™ map of the set of 1900 patent documents in which the words ‘gold’ and ‘catalyst’ appear in either the title, the abstract or the claims. On the ‘landscape’ created, heights of peaks indicate the relative level of patent activity i.e. the white ‘snow capped peaks’ indicate a very large number of patents in a particular technology area. Patents relating to similar technology areas are located together on the map, whilst those with little or no discernable link are positioned apart on the map. There are no horizontal or vertical axes in a quantitative sense.

A number of broad themes stand-out within particular sections of the map, namely:

- Exhaust gas cleaning (this embraces automotive and industrial applications)
- Fuel cells (this region of the map includes gold catalysts for PROX and WGS reactions as well as electrocatalysts)
- Hydrogen peroxide (for local production where it is to be used)
- Olefin production (many of the major chemical companies have patented gold-based catalysts for this application), and removal of impurities (dienes, alkynes) that poison polymerization catalysts
- Precious metal precursors (this relates to preparation of gold catalysts using precursors)

Each of these is known to be of particular interest to the academic research community as well. Of course, care must be taken in interpreting this form of data because it can be distorted by large numbers of ‘routine’ patents, i.e. where gold is listed as a *possible* component of a catalyst formulation with little or no likelihood of it being seriously used in such an application. For example, many platinum-based catalyst patents include mention of gold as a possible constituent, although in practice, it is not used as yet in these commercial formulations. Patents are nevertheless an effective source of market intelligence although older patents may not necessarily indicate continued commercial interest if they have not been maintained by the applicant.

Because the map is generated on the basis of the numbers of patents relating to certain themes, it is possible to overlook key technology areas that have been defined by only a few key patents (for example, mercury oxidation and some selective oxidation reactions) or no patent has yet been published (e.g. ground water purification from chlorinated hydrocarbons).

The software used in the present example also allows further interrogation of the dataset, including the nominated patent assignee. Those companies and organisations that have most heavily patented in gold catalysis are, in decreasing order, BASF, Celanese Corp, Toyota, Dow Chemical, Du Pont, Nippon Shokubai, BP plc, AIST, Japan, Arco Chemical and Institut Français du Pétrole. However, whilst it is useful to understand the broad patent landscape for this technical field, it is more instructive to analyse key patents in greater depth. A number of key patents related to gold catalysis have been identified as important milestones in the more widespread application of gold catalysis, table 1.

The list in table 1 is necessarily selective and there are other patents in these (and other) fields by other well-known companies and organisations. Along with the published scientific literature, it does serve to illustrate the considerable interest in exploiting gold-based catalysts for significant applications based on these reactions. The following sections examine these in more detail, but we could also have considered

- Vinyl acetate monomer (there are a large number of patents relating to commercial formulations and their production)



Figure 1. A patent map for published patents related to gold catalysis (1996–2005) [16,17].

other patented technologies such as odour removal, automotive pollution control, oxidation of ethene to carbon dioxide, selective oxidation of propene to propene oxide and of saturated hydrocarbons such as cyclohexane to the nylon intermediates cyclohexanol and cyclohexanone and conversion of ethyne to vinyl chloride.

### 3. Chemical synthesis

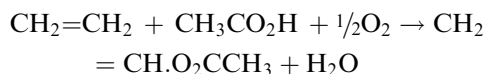
#### 3.1. Vinyl acetate monomer (VAM) production

There is a need for VAM for large scale uses in emulsion-based paints, wallpaper paste and wood glue. There are a number of well-established commercial processes for the manufacture of vinyl acetate monomer

Table 1  
Important patents in gold catalysis

Reaction or Topic	Patent Number/Title	Year	Patentee	Comments
Vinyl Acetate Monomer	USP 5808136	1996	Degussa	Fixed bed process
	EP 0 654 301 A1	1994	BP plc	Fluidised bed process
Methyl Glycolate	JP 938776	2003	Nippon Shokubai	Synthesis from ethylene glycol and MeOH
Glucose to Gluconic acid Water Gas Shift	WO 2004/099114 A1	2004	SüdZucker Aktiengesellschaft	Ambient temperature ?
	WO 2005/005032 A2	2005	Chevron Inc	Good durability
	WO 2005/087656 A1	2005/2006	Johnson Matthey	Au/CeO <sub>2</sub> /ZrO <sub>2</sub> in fuel cell stack
	WO 2006/046033 A1		Johnson Matthey	
CO oxidation	JP 60238148	1985	Kogyo Gijutsin, Japan	
	WO 2005/030382 A2	2005	3 M	Respirators
	WO 2006/074126 A2	2006	3 M	
	EP 1 570 895 A2	2003	Delphi Inc	Automotive
Air cleaning	EP 1 043 059 A1	2000	Toyota	Automotive
	WO 2005/079875 A1	2005	Givaudan SA	Air purifier
	WO 2004 112958 A1	2004	Carrier Corpn	VOC's & CO
	WO 2004/002247 A2	2004	Rhodia	Cigarettes
Water purification	JP 06142660 A	1994	Nippon Shokubai	Removal of nitrogen compounds
Mercury removal	US 6,136,281	2000	Tennessee Valley Authority	Power plant effluent
Hydrogen purification	EP 1 209 121 A1	2002	Haldo Topsoe	PROX
	US 2006/0165576A1	2006	Samsung SDI Co.	
	WO 2005/59631	2005	Anglo-American	
Fuel cell electrocatalyst	WO 2006/021740	2006	Johnson Matthey plc	Pt-Au-X
Hydrogen peroxide	WO 02/064500 A2	2002	ARCO Chemical	For in situ use

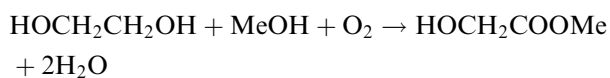
from ethene, acetic acid and oxygen using Au-Pd catalysts [20, 21]:



The chemical technologies for these processes were developed in the 1960s, and have been operated commercially since the 1970s and today VAM is produced with high selectivity and high space time yield in many plants around the world. Worldwide VAM capacity is currently ca 5 million metric tonnes per year, and is expanding: 80% of which is produced via the ethene route. VAM catalyst consumption is several hundred tonnes per annum. Potassium acetate is widely used as a co-catalyst and BP have recently introduced a fluidized bed process [22]; the other processes use fixed beds. The increased space time yield now expected requires efficient heat removal. The catalyst is durable and typically lasts for between one and two years. Since water is a by-product of the reaction, there could be a liquid phase aspect to the process as well as gas phase which may help to increase the catalyst durability. The presence of gold leads to a three fold increase in space time yield compared with use of palladium alone (150 vs 50 g / l / h) and the presence of gold clearly therefore has commercial importance [23]. The bulk alloy is Pd<sub>0.8</sub>Au<sub>0.2</sub> but on the surface the composition is richer in gold, Pd<sub>0.45</sub>Au<sub>0.55</sub> [24].

### 3.2. Methyl glycolate pilot plant

Recently a liquid-phase air-oxidation process has been developed by Nippon Shokubai in Japan for the one-step direct production of methyl glycolate from ethylene glycol and methanol using a gold catalyst.:



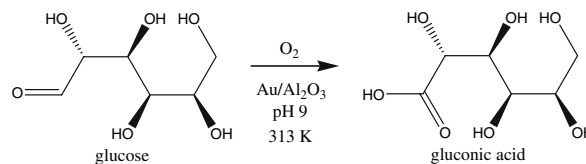
Methyl glycolate is used as a solvent for semi conductor manufacturing processes, as a building block for cosmetics and as a cleaner for boilers and metals.

A pilot plant demonstration, with a capacity of tons per month, successfully showed that this can be run as a clean and simple continuous process with the product obtained in high purity. The catalyst used for this reaction, as given in the associated published paper, was Au-Pb/Al<sub>2</sub>O<sub>3</sub> and the conditions used were 90 °C and 0.1 – 5 MPa [25–27]

### 3.3. Conversion of glucose to gluconic acid

Gluconic acid is an important food and beverage additive, and it is also used as a cleansing agent and is made on the 60, 000 tonnes per annum scale. Work at

the Federal Agricultural Research Centre (FAL), at Braunschweig, Germany has demonstrated that the oxidation of glucose to gluconic acid can be maintained at high activity and selectivity using a stirred tank reactor for up to 110 days [7], with catalysts prepared by deposition precipitation with urea and incipient wetness methods:



3.8 tonnes of gluconic acid can be obtained per gram of gold in 70 days [28]. The catalyst was thus shown to have excellent long term stability. Südzucker Akt. [29] have filed a patent covering use of gold catalysts for this conversion.

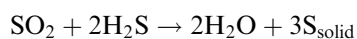
### 3.4. Water-gas shift (WGS)

WGS makes important contributions to the production of hydrogen for a number of processes in petroleum refineries as well as in chemical synthesis and is the usual means for the production of hydrogen for fuel cells. During investigations aimed at reducing CO levels in hydrogen feeds for fuel cells (see Section 5.2), a GROW project involving collaboration between the World Gold Council, Johnson Matthey and the Queen's University Belfast found that Au/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts are highly active for the water gas shift reaction and produce hydrogen from water at as low a temperature as 100°C, a much lower temperature than currently employed with copper/zinc catalysts. Characterization of these catalysts indicated that they contain gold in an ionic form but a careful review of WGS publications [30] strongly points to the active form during reaction being zerovalent gold, and a key feature of a 'stable' active catalyst is strong interaction between gold and the oxide support surface. Kinetic studies of the reaction show that it is positive order in CO and H<sub>2</sub>O but negative order in CO<sub>2</sub> and H<sub>2</sub> and that the reaction mechanism may be significantly different from that for a Pt/CeO<sub>2</sub> catalyst [31]. The fact that the Au/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts show 20% CO conversion at 100°C is particularly noteworthy. Johnson Matthey have filed three recent patents on WGS [32–34], the first of which covers use of ceria-zirconia as a support for suitable gold catalysts and the second the use of a gold-based WGS catalyst within a fuel cell membrane electrode assembly. The third claims use of two reactor zones joined together with the first monolith containing Au/CeO<sub>2</sub>/ ZrO<sub>2</sub> and the second Pt/ CeO<sub>2</sub>/ ZrO<sub>2</sub>, thus combining the advantages of both systems in a WGS

reactor for producing hydrogen without any cooling between the two stages.

In a Chevron patent [35] 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 ZrO<sub>2</sub> (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, i.e. this catalyst had promising activity and durability characteristics.

This patent provides evidence of advantages for the presence of sulfur in catalysis by gold. This is interesting because doubts have been expressed about gold catalysts being subject to sulfur poisoning. Further evidence of resistance to sulfur poisoning is provided by the results of Lui *et al.* (Brookhaven National Laboratory, USA) [36]. It was found that Au/TiO<sub>2</sub> is five - ten times more active than pure titania for the reduction of SO<sub>2</sub> by CO and also five - ten times more active for the Claus reaction:



Hydrodesulfurization reactions are also catalysed by gold [37] 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.

## 4. Pollution control applications

### 4.1. Respirators for protection from CO poisoning

Respirators are required in emergency situations for protecting firefighters and miners from carbon monoxide poisoning near fires and boilers, etc in both domestic and working situations and several companies and organizations are known to be developing systems based on gold catalysts, working at ambient temperatures [38, 39]. For example, Union Chemical Laboratories in Taiwan have developed masks for fire fighters which last for up to 100 h and which operate at room temperature: the gold particle size is 2 nm on oxide supports. Studies on carbon monoxide oxidation over gold catalysts (supported on Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) in real air confirm that they are useful for the removal of carbon monoxide from both low (10–100 ppm) and high concentrations (10,000 ppm)[2, 40, 41].

In the 20 years since Prof Haruta's initial dramatic breakthrough with his observation of high activity for oxide-supported nanoparticulate gold catalysts for CO oxidation at room temperature and below, there has been much effort on optimizing solution methods for

preparing gold catalysts, a simple reproducible, cost effective method of forming gold nanoparticles and depositing them on a wide variety of substrates to make reproducible highly active oxidation catalysts was proving elusive.[42]. The 3M company in Minnesota, USA has now found that very active gold nanocatalysts can be prepared via physical vapour deposition (PVD) using equipment originally designed for manufacturing electronic printed circuits[43, 44] on a wide range of supports, including some that are water soluble. The method provides the advantages of low cost, superb reproducibility, removal of the need for washing and thermal treatment steps, and there are no toxicity hazards. It takes only 2 – 3 h to make 400 ml catalyst and there is minimal loss of gold. Such 0.7% Au/TiO<sub>2</sub>/C catalysts are stable for two years if kept in a canister for use in respirators. Such a storage life is important for such life-critical applications.

### 4.2. Pollution control in living spaces

Gold catalysts are highly active for the oxidation of many components in ambient air at low temperatures, particularly carbon monoxide and nitrogen-containing malodorous compounds such as trimethylamine. This ability offers scope for applications related to air quality improvement and control of odours, be they in buildings, transport or other related applications such as gas masks. This a very important issue and the scope here for commercial applications is very large: significant patents have been published [2, 45–47]. It is particularly advantageous that gold's catalytic activity is often promoted by moisture. Prototype products that use gold catalysts for low temperature air quality control are now appearing in the public domain [48, 49]. Philip Morris Products SA have a patent [50] claiming use of Au/CeO<sub>2</sub> for oxidizing CO at room temperature. It is believed that the market for this type of product will grow rapidly in the coming years.

Air-cleaning devices are needed for removing carbon monoxide and trace amounts of VOCs and ozone from ambient air indoor office space (due to smoking, etc) and in confined spaces such as submarines or space crafts on long missions [45]. The Carrier Corporation (US) has a patent [51] claiming use of Au/TiO<sub>2</sub> photocatalytic/thermocatalytic coating for simultaneously oxidising VOCs and carbon monoxide. Rhodia GmbH of Germany has a patent for a Au/CeO<sub>2</sub>/ZrO<sub>2</sub> catalyst for the oxidation of carbon monoxide and treatment of tobacco smoke and polluted air and for use as a filter in cigarettes [52].

Au/Fe<sub>2</sub>O<sub>3</sub> is also a catalyst for ozone decomposition and simultaneous elimination of ozone and carbon monoxide at any ratio in the presence of oxygen at ambient temperature [53]. This catalyst is suitable for use in severe conditions such as relatively high ozone concentration, and large space velocity. It also shows a

high room temperature activity and good resistance to moisture.

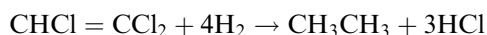
Incinerator exhaust gases can contain a huge variety of pollutants, such as dioxins, VOCs, hydrocarbons, nitrogen oxides, carbon oxides and amine derivatives. Due to the variety, it would be unreasonable to expect a single-component catalyst to achieve high catalytic performance for all of the exhaust gas pollutants. However, it has been shown that if several supported single noble metal catalysts are encouraged to work in synergy, the overall catalytic activity can be greatly improved [54]. Consequently, a ternary component noble metal catalyst (consisting of gold supported on  $\text{Fe}_2\text{O}_3$ -Pt/ $\text{SnO}_2$ -Ir/ $\text{La}_2\text{O}_3$ ) achieved good results for purifying typical exhaust gases emanating from incinerators even at 423 K [54, 55].

Odour-producing substances, such as trimethylamine, and toxic compounds such as dioxins can be oxidatively decomposed over Au/Ni $\text{Fe}_2\text{O}_4$  at temperatures below 373 K, and a mixed Ir/ $\text{La}_2\text{O}_3$ /Pt $\text{SnO}_2$ Au/ $\text{Fe}_2\text{O}_3$  catalyst at 423 K respectively where it has been demonstrated by Osaka Gas Company that lower temperatures can be used if gold is present in the catalyst [5, 56–66]. Au/ $\text{Fe}_2\text{O}_3$  supported on a zeolite washcoated honeycomb, has been used commercially as a deodorizer in Japanese toilets since 1992 [55, 56].

#### 4.3. Water purification

Chlorinated hydrocarbons are major pollutants of groundwater. For example, trichloroethene is used to degrease metals and electronic parts in the automotive, metals and electronic industries and also in chemicals production, textile cleaning and consumer products. Recent research at Rice University's Center for Biological and Environmental Nanotechnology has revealed that bimetallic gold-palladium nanoparticles provide an active catalyst to break down trichloroethene (TCE), one of the most common and poisonous groundwater pollutants. TCE has been linked to liver damage, impaired pregnancy and cancer. The new catalyst works better than the carbon filters currently in use because it converts the TCE to non-toxic components instead of just trapping it in the filter [67]. It also performs better than iron because it is not consumed in the reaction and, thus, can be used repeatedly; in contrast, iron catalysts produce toxic intermediate chemicals such as vinyl chloride.

Palladium catalysts have previously been shown to remove trichloroethene and other chlorinated compounds from water effectively at room temperature using hydrogen, but catalyst cost is a significant barrier to widespread adoption. The reaction involved is:



In order to use less metal, Dr Wong's team at Rice coated small amounts of Pd atoms onto gold (Au) NPs.

The increase in Pd catalytic activity was expected, but the dramatic two orders of magnitude enhancement (from 47 L/gPd/min to ~2300 L/gPd/min) was an exciting surprise [68, 69]. Gold is more expensive than palladium but, since the Pd-Au nanoparticles are so much more active than pure Pd particles of the same size, they are more cost effective. This nanomaterial opens up tremendous opportunities in groundwater clean-up, e.g., remediation of other compounds like arsenate (a severe problem in southeast Asia) and perchlorate, and inexpensive portable water purification units. The Rice group is currently studying how the gold increases the Pd catalytic activity (and also resistance to poisoning); experiments suggest geometric and electronic effects are responsible.

Another indication that gold catalysts may be useful in water purification applications is the recent work reported on nitrate removal [70]. Trimetallic Pd-Sn-Au catalysts supported on silica are very active and selective in nitrate and nitrite reduction. The addition of gold improves the stability and selectivity towards nitrogen formation compared with the parent Pd-Sn catalyst.

Nippon Shokubai have a patent for treatment of waste water containing nitrogen compounds [71] with an oxide catalyst on which gold and optionally platinum are supported, and we believe that more patents will soon emerge on removal of other water pollutants including chlorinated hydrocarbons and nitrates, as this is a major area of concern in terms of environmental damage and, hence, opportunity for commercial application for gold.

#### 4.4. Mercury oxidation

The US is relying increasingly on the use of coal to produce electrical power and significant levels of mercury occur in the gaseous emissions from these power plants. Control of mercury, which has been linked to Alzheimer's disease and autism, is expected to be the subject of legislation by the US Environmental Protection Agency (EPA). The EPA will impose limits on mercury emissions from coal-fired boilers in the utilities industry. Current mercury control techniques used in the industry include the use of flue-gas desulfurization (FGD) units and, as a result of mercury measurements around these units, it is known that oxidized and not elemental mercury is removed by the FGDs. Thus, one method to increase mercury removal by FGD units is to introduce a catalyst to enhance the oxidation of mercury [72]. Mercury measurement studies [73] led to the discovery that a gold-coated sand sample in a simulated flue-gas environment absorbed elemental mercury until an equilibrium was established and desorption of oxidized mercury began. Individual components of the simulated flue-gas were evaluated for their effect on the oxidation of mercury. Of the components, nitrogen



dioxide and hydrogen chloride were primarily responsible for the mercury oxidation over gold; thus, it is not yet clear whether gold is acting through a truly catalytic mechanism in this instance, but it was the most active of the catalyst materials evaluated.

This is another area of environmental concern with major commercial potential for gold, not just in the USA but worldwide.

## 5. Hydrogen purification and fuel cells

### 5.1. Hydrogen purification

It is well known that the presence of carbon monoxide in the hydrogen supplied to fuel cells causes poisoning of the Pt catalysts inside the PEM cell. 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 CO<sub>2</sub> reaction than for the H<sub>2</sub> to H<sub>2</sub>O reaction and removal of the CO prevents poisoning of the Pt fuel cell catalyst [74]. The presence of sodium in the gold catalyst decreases the TOF for Au/Fe<sub>2</sub>O<sub>3</sub> and should therefore be thoroughly removed by washing [75]. Au/ZrO<sub>2</sub> obtained from Au<sub>0.5</sub>Zr<sub>0.5</sub> alloy gives good selectivity for oxidation of CO in the presence of H<sub>2</sub> in the 50 – 70°C range [76], and CO conversions of 99.8% have been obtained at 80 °C using 5% Au/Fe<sub>2</sub>O<sub>3</sub> calcined in two stages (at 400 and 550 °C) [77] but gold catalysts can also perform the PROX reaction efficiently at ambient temperatures.

A promising recent example of this has been provided by Project AuTEK [78] with a new system for hydrogen purification for PEM fuel cells, tradenamed *AuroPureH<sub>2</sub>*. It is designed to purify on-board cheap hydrogen on vehicles, drawing the hydrogen feed for the fuel cell directly from a cylinder. The Au/TiO<sub>2</sub> catalyst is very selective for CO oxidation and can remove high levels from the hydrogen. The low (ambient) operating temperature gives high selectivity and no additional energy is required to heat the reactor. Fuel efficiency is essentially maintained and this low cost, simple and practical system allows lower Pt loadings for the fuel cell anode, reducing cost whilst not adding significantly to the weight and volume of the fuel cell system. Complete removal of the CO in the hydrogen avoids the need for PtRu or PtMo anodes.

The *AuroPureH<sub>2</sub>* system removes carbon monoxide to below 1 ppm (from 10 – 2000 ppm CO in H<sub>2</sub> with a 1 – 2 % air bleed) [79]. Therefore, it outperforms the PtRu and PtMo CO tolerant technologies. The system design is simple, and it is planned to develop this innovative technology into a commercial product in collaboration with commercial partners. An example of the use of this new technology on the performance of a PEM fuel cell is given in graphical form in Figure 2 for hydrogen feeds containing 1000 ppm carbon monoxide.

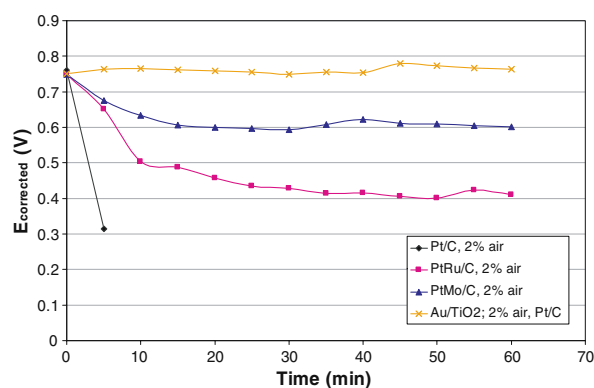


Figure 2. Plots showing comparison of CO tolerance results (1000 ppm CO, 0.5 A.cm<sup>-2</sup>, 1.5 times stoichiometric hydrogen flow rate, SV over 3 wt% Au/TiO<sub>2</sub> catalyst = 250,000 ml.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup>, Au-based catalyst chamber at 25°C, fuel cell at 80°C, 30 psi [78]. Reproduced by permission of Mintek, the copyright holder.

Table 2 shows the performance loss for the four technologies investigated. The oxygen concentration is limited by an air bleed and has a very small effect on fuel efficiency. It has now been demonstrated that the *AuroPureH<sub>2</sub>* system achieves complete removal of up to 2000 ppm carbon monoxide in hydrogen streams over a 3 wt% Au/TiO<sub>2</sub> catalyst at a space velocity of 850,000 ml.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup> with a 2% air bleed and at a gold cost of less than 1% of the US DoE stipulated cost target of \$45/kW for vehicular fuel cells.

A 0.9% Au/TiO<sub>2</sub>/C catalyst made using the PVD 3M PVD method (see Section 4.1 above) has also been used for PROX and CO has been removed in hydrogen streams down to < 1 ppm (at < 70°C) [11]. There are a number of other PROX patents including those by Haldor Topsoe A/S, Denmark [80] claiming use of a gold on MgAl<sub>2</sub>O<sub>4</sub> spinel catalyst for the preferential oxidation of CO and/or methanol in hydrogen-containing feedstocks. It has high stability in the presence of water and CO<sub>2</sub> and shows selectivity towards oxidation of CO in hydrogen. More recently, Samsung SDI Co Ltd, Korea [81] claim a PROX catalytic system for CO removal which includes a gold catalyst (on carbon or oxide support) and a base metal co-catalyst with a redox potential in contact with an aqueous phase and a fuel cell system using this. It is highly efficient at removing CO at 90°C or less (optimum at 60 – 80°C) and the water in the system can act as a temperature buffer.

Table 2  
Performance losses for four technologies represented in Figure 2\*

System	Performance Loss (mV)	Performance Loss (%)
Pt/C	Tripped below min V of 0.25 V	100
PtRu/C	399	45
PtMo/C	147	20
Pt/C + Au/TiO <sub>2</sub>	0	0

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There is a further patent from Anglo American Research Labs [82] and an earlier one by AIST, Japan [83].

### 5.2. Fuel cells

Fuel cells are energy generators which provide a combination of high efficiency and with low pollutant emissions. They are based on the direct electrochemical oxidation of hydrogen or hydrocarbon fuels to provide an electric current, and at the same time form water [14, 45, 84] which can be a useful by-product in space travel and submarines. Fuel cells have been developed for a wide range of applications including stationary generators, cars and buses, industrial vehicles and small portable power supplies for mobile telephones and laptop computers, each of which represents a substantial market. After decades of development and large-scale trials, fuel cell generators are now entering commercial service to provide electricity and heat for individual homes, or district schemes. In addition, virtually all the world's major vehicle manufacturers are demonstrating electrically propelled passenger vehicles or municipal buses [85].

The application of gold as an electrocatalytic component within the fuel cell itself includes the historical use of a gold-platinum electrocatalyst for oxygen reduction in the Space Shuttle/Orbiter alkaline fuel cells (AFC) [86], and the recent use of gold for borohydride oxidation in the direct borohydride alkaline fuel cell (DBFC) [87, 88].

Electrocatalysts with lower cost, improved carbon monoxide tolerance and higher performance are needed for the membrane/electrode assemblies of other low temperature fuel cells (polymer electrolyte membrane, PEM and direct methanol, DM). With gold presently approximately half the cost of platinum on a weight-for-weight basis, research programmes are evaluating gold as a potential electrocatalyst component, particularly as part of a bimetallic system with platinum group metals. Results reported on gold and gold-platinum as potential fuel cell electrocatalysts include the synthesis, assembling, and thermal treatment of shell-capped gold and gold-platinum particles in the 2–5 nm size range. The electrocatalytic oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) activities of the gold and gold-platinum nanoparticle catalysts were compared with commercially-available Pt/C and Pt-Ru/C catalysts. The gold-platinum catalysts with Au:Pt > 7:3 and 10–25% metal loading exhibited at least comparable, and in some cases much higher, catalytic activities than platinum (ORR) and platinum-ruthenium catalysts (MOR) in alkaline electrolytes [89–91].

The micro-fuel cell developed at QinetiQ, Europe's largest science and technology organisation, is one of the first uses of a carbon-supported gold electrocatalyst for fuel cell applications [45, 92]. QinetiQ has recently

developed direct liquid fuel cells based on alkaline electrolytes. As well as having improved electrocatalysis and lower methanol permeation rates than methanol fuel cells, the alkali environment stabilises several alternative fuels which decompose in neutral or acidic media. Fuel cells based on sodium borohydride (direct borohydride fuel cell, DBAFC) have been shown to have good energy storage and activity. QinetiQ have now developed a prototype based on this fuel and are developing their system as a potential replacement for rechargeable batteries for mobile and portable electronics. It is possible that the DBAFC in this type of application would be rechargeable simply by replenishing the discharged fuel solution.

The QinetiQ micro-fuel cell consists of a cylindrical unit cell in which the interior of the cell is utilised as a fuel reservoir, and uses a 40 wt% Au/C (Vulcan XC72) catalyst manufactured by E-Tek Inc, USA. Fuel is fed to the anode catalyst via holes in the inner cylinder which also acts as the anode current collector. Gold is used as the anode catalyst due to complications in the anode reaction mechanism, since borohydride fuel solutions decompose to produce hydrogen in the presence of platinum or ruthenium. Gold is beneficial because it is relatively unreactive to this decomposition reaction while being suitably active to the desired borohydride oxidation reaction.

There could be opportunities to exploit the properties of gold and gold-platinum group metals catalysts, particularly for low temperature proton exchange membrane (PEM) fuel cells, which are one of the most widely developed forms of generator and also the most susceptible to poisoning by impurities in the hydrogen [85, 93]. Platinum group metals are currently used for both anode and cathode catalysts in most commercial PEM fuel cells, but the tendency for poisoning of the platinum anode by even a few ppm carbon monoxide contaminant in the hydrogen remains a major technical issue.<sup>30,31</sup> Work is now emerging [89, 94, 95] that investigates the potential benefits of alternative gold-platinum group metal bifunctional catalysts. This is based on the premise that the use of gold-platinum nanoparticles could generate unique bifunctional catalytic properties with platinum acting as the catalyst for the main fuel cell reaction and gold assisting via the oxidation of carbon monoxide under the low operating temperatures of the fuel cell.

This approach would also potentially have two other advantages over current technology. Firstly, if platinum loadings could be reduced, it could produce a welcome reduction in the capital cost of fuel cell catalysts. In recent years, prices for platinum have significantly exceeded those for gold [12]. Cost remains a significant barrier to more widespread commercialisation of fuel cell technology and a reduction in catalyst cost and an increase in the availability of suitable catalysts are factors identified as key objectives throughout the industry.



The second advantage from incorporation of gold into fuel cells would be the useful enhancement in electrical conductivity that could be derived, due to the lower electrical resistivity of gold compared with platinum [85]. There are patents on the use of gold-platinum particles as fuel cell catalysts [96–98].

Electricity has been produced by catalytic oxidation of carbon monoxide using gold catalysts at room temperature, using gold nanotubes in polycarbonate membranes [99, 100]. These gold nanotubes exhibit catalytic activity for carbon monoxide oxidation at room temperature, and this activity is enhanced by the presence of liquid water, promoted by increasing the pH of the solution, and increased using hydrogen peroxide as the oxidizing agent. The rate can also be increased by depositing potassium hydroxide within these nanotubes. These rates are comparable with those found in heterogeneous catalysis studies with gold nanoparticles on oxide supports, which suggests that the high activity of the oxide-supported catalysts may be related to the promotional effect of hydroxyl groups. The observed rates are faster than for conventional processes operating at 500 K or higher for the conversion of carbon monoxide with water to produce hydrogen and carbon dioxide via the water gas shift (WGS) reaction. The elimination of the need for WGS means that there is no need to transport and vaporize liquid water in the production of energy for portable applications. The process can use carbon monoxide-containing gas streams from the catalytic reforming of hydrocarbons to produce an aqueous solution of reduced polyoxometallate compounds that can be used to generate power. The reduced polyoxometallate can be reoxidized in fuel cells that contain simple carbon anodes.

## 6. Hydrogen peroxide production

The market for hydrogen peroxide is very large ( $\sim 1.9 \times 10^6$  tonnes  $\text{yr}^{-1}$ ); and there is a great economic incentive to find a means of making it where it is to be used, so as to avoid the heavy cost of transporting a hazardous chemical. It is widely used, e.g., for bleaching textiles and paper pulp, as an oxidising agent in chemicals manufacture and in rockets and other military applications as well as the destruction of cyanide in mining operations. Its production by the anthraquinone route is only economic on a large scale, but it is often required on a much smaller scale. Theoretical calculations [101] and experiments [102–104] have both shown that its formation is favoured over gold surfaces. Au/TiO<sub>2</sub> gave high peroxide productivities when dispersed in methanol or methanol-water at 275 K [105]. Higher temperature caused the hydrogen peroxide to decompose. Operating conditions were 3.7 Mbar with 1:2 hydrogen: oxygen ratio. The combination of palladium with gold worked better; a 1:1 ratio was usually used.

Extensive characterisation involving STEM/EDX has indicated that in the working catalyst there was a partial or complete palladium shell overlying a gold core. There are several patents on use of gold catalysts for direct synthesis of hydrogen peroxide dating from the 1990s. One from Sumitomo [106] covers use of gold with a platinum group metal, and there is a more recent one from Arco Chemical, USA claiming use of a gold on oxide support (TiO<sub>2</sub> or TiO<sub>2</sub>/silica) in a liquid phase reaction of hydrogen and oxygen in an oxygenated solvent such as water at 20–60°C. [107]. There is also a Mitsui Toatsu Chem. Inc. patent [108] describing use of a gold fine particle catalyst under pressure in aqueous acid solution, and another from Solvay using a supported Pd-Au alloy catalyst [109]. Interlox Int. SA describe a method for preparing hydrogen peroxide from hydrogen and oxygen in an aqueous medium using Pd/Au alloy or Pd/Ir or Pd/Rh [110]. It can therefore be concluded that Au and Au-Pd catalysts provide an effective basis for manufacturing hydrogen peroxide from hydrogen and oxygen for 'in situ' local production.

## 7. Commercialisation: some important factors

If gold catalyst-based technologies are to see commercial application, a number of factors need to be considered besides the technical attributes of activity and selectivity. As discussed earlier, chief amongst the technical attributes still required is durability in gas-phase applications. There is already good evidence that gold catalysts can achieve adequate durability in the liquid phase. Full scale production and pilot plants have been run successfully for the production of vinyl acetate (Section 3.1) and methyl glycolate (Section 3.2) respectively. Sufficient stability now needs to be established more widely for gas phase operations including environmental and fuel cell applications, but there are already promising signs, including the use of physical vapour deposition (PVD) of metallic gold as a preparative technique, thus avoiding the use of the H<sub>2</sub>AuCl<sub>4</sub> used in many of the routes using soluble gold compounds, leading to the presence of chloride residues which promote sintering of the catalysts. Nevertheless there are new aspects of preparative approaches using solutions such as those reported in this Special Issue [111], showing that careful choice of mixed oxide supports and conditions used for pre-treatment, washing and storage can produce stable catalysts. Au/SnO<sub>2</sub> catalysts suffer initial deactivation for CO oxidation followed by an increase in activity for time on stream. The high activities of gold catalysts is firmly established, and the achievement of long term durability is now a more important objective than preserving their high initial activities. Increased financial investment is now required in order to perform the durability tests over much longer periods than has been possible to date, and much of this

needs to be performed in industry/ There are good indications that durability can be achieved.

Another factor is the manufacture and supply of catalysts in commercial quantities. Until quite recently, potential end-users have experienced difficulty in sourcing trial quantities of gold-based catalysts, as a pre-commercial supply has not been widely available. This issue has now been addressed. Firstly, in 2002 World Gold Council commissioned the production of three gold reference catalysts, Au/TiO<sub>2</sub>, Au/Fe<sub>2</sub>O<sub>3</sub> on alumina beads, and Au/Fe<sub>2</sub>O<sub>3</sub> from Sud Chemie in Japan, under the guidance of Prof. Masatake Haruta and colleagues at Japan's AIST. A fourth reference catalyst, Au/C, was later made available, having been prepared under the guidance of Prof. Michele Rossi from the University of Milan. To date, over 150 samples of catalyst have been supplied to universities and industrialists. Up-to-date information on the catalysts and their availability is readily obtained [112]. Recipients of these catalysts are encouraged to share their characterization and activity results, thus providing valuable benchmarking comparisons between the groups using them.

Whilst the WGC gold reference catalysts have been used by some industrial companies to explore the applicability of gold to new end applications, they are not optimised for such a purpose. It is, therefore, exciting that during 2005, Project AuTEK at Mintek in South Africa produced custom-made gold catalysts using a new pilot plant and now has the capability to produce up to 20 kg quantities, available in a form suitable for industrial use in a range of applications. This is the first time that significant quantities of gold catalysts have been made accessible to potential new users.

In addition to the World Gold Council and AuTEK initiatives, it is encouraging that other major industrial companies are now publishing details of commercially orientated gold catalyst production methods [43]. This bodes well for the future of this exciting new field of catalyst technology, with commercial exploitation foreseen in the near to medium term [15, 113, 114]. Other important factors in realizing commercialization are economic. Firstly, as discussed earlier, gold is around half the cost of platinum and it is also available on a much larger scale than the PGMs, so any new industrial demand of several hundred tonnes is easily accommodated without impacting on its price stability (in contrast to the PGMs) [12].

One area of application not discussed in this paper is the potential use of gold catalysts in automotive pollution control where gold demand could attain this order of magnitude, and, for example, Toyota have patented mixed gold/alkali and alkaline earth metal oxides for automobile exhaust gas purification [115]. As discussed earlier [12, 14] the low temperature light off characteristics could solve the problem of the 'cold start' situation

and as gold catalysts have promising DeNO<sub>x</sub> characteristics [116] their use in DeNO<sub>x</sub> has also been investigated using 'zeolite supported by Co or Cu by ion exchange and gold [117]. There are a number of other patents claiming formulations for removal of NO<sub>x</sub> in automotive exhaust, e. g. Au-Pt on TiO<sub>2</sub> in oxidizing atmosphere in presence of excess oxygen and reducing agent [118] and gold complexed with a transition metal, e.g. cobalt oxide, to reduce nitrogen oxides and oxidize carbon monoxide [119]. Blue Planet Ltd, Korea have patented a plasma/gold catalyst system for removing NO<sub>x</sub> from diesel engines for air quality improvement in Seoul City [120].

In general, the process of application of scientific discoveries by industry has several stages: (1) discovery of the effect, (2) establishing reproducibility for the results, (3) defining area/conditions/limits where this effect exists, (4) understanding the mechanism of the effect, (5) using the accumulated knowledge to optimize the product or process and (6) successful use by industry [7]. At present gold catalysis is at stages (3) / (4), but already we can suggest suitable gold catalysts for industrial developments, which can later be substituted by optimized systems.

Nevertheless there is already evidence of real activity of type (5) and the facility for production of catalysts for respirators exists at 3 M, and their patents [43, 44] are based on extensive R&D. The use of gold catalysts to oxidize the mercury effluent from coal-based electricity generation plants looks promising and its implementation could be hastened by legislation of the type which led to the introduction of platinum group metal catalysts to meet automotive emission control legislation introduced in the 1970s. The continuing [121] and widespread activity on using gold catalysts for PROX leads to the belief that this will be commercialized soon, especially as the use of gold catalysts allows smaller fuel cell processors and hence capital saving on plant cost. The FAL work on the liquid-phase oxidation of glucose to gluconic acid described in Section 3.3 indicates that this could be commercialized soon since the catalyst is very durable; and other chemical processes which could be developed soon include ethylene glycol to methyl glycolate where promising results have been obtained on a pilot plant (Section 3.2), and hydrogen peroxide synthesis (Section 6).

However, it is only when the gold suppliers and industry devote considerably more financial support to R&D in gold catalysis than is currently available that we will see commercial products emerging at the rate which the potential indicated by the scientific progress to date warrants. In this application context, it is worth noting that platinum-based catalysts only succeeded in meeting commercial technical requirements after considerable R & D effort was expended by the major precious metal companies. If commercial exploitation of gold catalysts is to succeed in areas such as automotive pollution control

and fuel cells, similar amounts of focused R & D expenditure need to be applied. That is not evident at present!

## 8. Conclusions

Gold is a unique catalyst in several ways and its ambient temperature activity, in particular, opens up new application opportunities. Indeed, the range of commercially-interesting chemical reactions where gold performs well is substantial and increasing.

Patent activity is a good marker of the commercial interest being shown in exploiting gold catalyst technology and patent mapping is a useful tool for determining which sectors have strong commercial prospects for exploitation. In this context, we have reviewed patent activity in this area and shown what progress is being made in selected areas.

Both technical and economic factors that impact on successful exploitation of the science and technology of gold catalysis have been discussed. In particular, the need for improved catalyst durability is highlighted, with availability of commercial catalyst supply also important. Another factor that could inhibit successful application is the lack of a sufficient level of investment in applications R&D by industry and the gold suppliers. This lack of investment increases the risk of failure in achieving successful commercialisation in several application sectors, such as fuel cells and automotive, but there is the evidence indicated above that applications could nevertheless be developed soon.

This substantial increased investment in gold R&D is required to solve durability problems, enable cost-effective large scale production of catalysts, the building of new pilot and full-scale plants, and development of effective methods for recovering gold economically from spent catalysts.

If the investment in gold catalyst R&D is suitably increased, applications for gold will soon emerge!

## Acknowledgements

We thank the GOLD 2006 presenters who sent us their power point slides and Profs Geoffrey Bond and Robbie Burch for providing copies of their manuscripts prior to publication.

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