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Commercial aspects of gold catalysis

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Abstract

There is the potential to apply catalysis by gold in numerous commercial applications. These practical uses include catalysts for pollution and emission control, chemical processing of a range of bulk and speciality chemicals, the emerging 'hydrogen economy' for clean hydrogen production and fuel cell systems, as well as for sensors to detect poisonous or flammable gases or substances in solution. The purpose of this paper is to briefly review the major commercial opportunities to apply heterogeneous gold catalysis and to highlight those areas that are considered to merit particular attention. It is considered that all involved in this exciting field need to carefully consider both the durability of catalysts under representative operating conditions and viable methods of catalyst preparation, in order to commercially apply the new science that has developed in recent years.

Keywords: Au; Industrial application; Commercial; Pollution control; Chemical processing; Fuel cell; Low temperature

1. Introduction

Following the breakthrough research results of Hutchings [1] and Haruta [2], there has been a dramatic increase in the number of published papers concerned with gold catalysis. It has now been demonstrated that heterogeneous gold catalysts, when prepared in an appropriate manner, are highly active and selective for a number of reactions, often at lower temperatures than existing commercial catalysts. With further technology development, there is clearly the potential to apply catalysis by gold in practical commercial uses, most likely within four broad application areas:

1. pollution and emission control technologies;
2. chemical processing of a range of bulk and speciality chemicals;
3. the emerging 'hydrogen economy' for clean hydrogen production and fuel cell systems;
4. sensors to detect poisonous or flammable gases or substances in solution.

Already, the first known practical application for gold as a catalyst component within a major industrial process is well established, namely its use within a palladium-gold bi-metallic catalyst formulation which includes potassium acetate for the production of vinyl acetate monomer (VAM) from ethene, acetic acid and oxygen. The application of a gold catalyst in the production of VAM, an important intermediate used in the production of polyvinyl acetate, polyvinyl butyral and a variety of other polymers, followed many years of industrially focused research and patent activity [3,4]. The use of an Au-Fe_2O_3 catalyst on a zeolite wash-coated honeycomb has also been in use within Japanese toilet systems for the removal of odours since 1992 [5].

One of the potential advantages that the use of gold catalysts offer compared to other precious metal catalysts is lower cost and greater price stability, gold being substantially cheaper (on a weight for weight basis) and considerably more plentiful than platinum. Whilst the gold mining companies are undoubtedly keen to see substantial new gold demand generated through new commercial uses of gold as a catalyst, it is not envisaged that this additional demand will result in strains on gold supply and hence

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upward pressure on the gold price. This is an important consideration for industrialists who wish to see stable costs in their manufacturing processes.

Based on the current research efforts being devoted to gold, there is cause for optimism that many new practical applications for gold-based catalysts could emerge over the next decade. The authors believe that to turn this expectation into reality, both a focused *technology push* and a significant *market pull* are required. Thus, firstly researchers need to be pro-active in exploiting promising research results and communicating these to industry. In particular, they need to carefully consider two particular research aspects: durability of catalysts under representative operating conditions and commercially viable methods of catalyst preparation. Secondly, end-user industries and catalyst manufacturers need to be open-minded, pro-active and innovative when regarding the potential business opportunities that gold-based catalysts undoubtedly offer. The purpose of this paper is to briefly review the major commercial opportunities to apply heterogeneous gold catalysis and to highlight those areas that are considered to merit particular attention. Sensors based on gold catalysts are included in our list above because they represent an important technological area. We do not deal with this topic in detail, however, because although sensors are being developed for widespread applications in detection of gases, such as CO and NO_x, and estimation of various substances, such as glucose in the liquid phase, and in biosensors (see reference [6] for details), each sensor uses a very small quantity of gold and consequently, these developments will lead to comparatively small expansions in sales of gold.

2. Future applications for gold catalysts

2.1. Pollution and emission control

2.1.1. Low temperature air purification

It is now well known that gold catalysts are highly active for the oxidation of many components in ambient air at low temperatures, particularly CO and nitrogen-containing odour compounds, such as trimethylamine. This ability offers scope for applications related to air quality improvement and control of malodours, be they in buildings, transport or other related applications, such as gas masks. The scope here for commercial applications is very large and significant patents have been published [7,8]. It is particularly advantageous that gold's catalytic activity is often promoted by moisture. The major remaining technical hurdle to overcome before widespread application of this technology is deactivation of gold catalysts caused by the accumulation of contaminants on catalyst surfaces or sintering of the active components. Nonetheless, prototype products that use gold catalysts for low temperature air quality control are now appearing in the public domain. It is believed that the market for this type of product will grow rapidly in the coming years.

2.1.2. Catalytic wet air oxidation

The efficient and environmentally acceptable processing of wastewater is of important industrial and environmental concern. One technique of growing interest is the wet oxidation process, where the oxidation of organic compounds in an aqueous solution or in suspension by means of oxygen or air takes place at elevated temperatures and pressures, 180–315 °C and 2–15 MPa [9]. The organic material present is first converted into simpler organic compounds, which are then further oxidized to carbon dioxide and water. Catalysts provide the possibility of using milder conditions and 'catalytic wet air oxidation' (CWAO) processes studied to date have been based on Pt and Pd catalysts deposited on titania or titania–zirconia [9]. Gold catalysts could prove to be advantageous and the recent work by Besson et al. [10] reports preliminary results on the catalytic wet air oxidation of succinic acid as a representative organic compound using Au on TiO_2 at 190 °C and 50 bar air pressure, which shows encouraging performance for gold catalysts.

2.1.3. Mercury oxidation in coal-fired power stations

Control of mercury, which has been linked to Alzheimer's disease and autism, is expected to be the subject of legislation in 2004 by the US Environmental Protection Agency (EPA). The EPA is expected to impose limits on mercury emissions from coal-fired boilers in the utility 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. According to Meischen [11], mercury measurement studies 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.

2.1.4. Automotive emission control

Perhaps, the greatest commercial (but most challenging) opportunity for gold-based catalysts lies in the automotive industry. With over 50 million light vehicles produced per year, this is a huge market for the catalyst industry. Commercial three-way catalysts (TWCs) are based on

platinum group metals (PGMs), especially platinum, palladium and rhodium and over 200 tonnes per year of these metals are used in automotive catalysts, by far the largest catalyst application for the platinum group metals.

It is fair to say that catalyst systems based on the PGMs perform the task of emission control very well and are able to meet current legislative emission targets. Many aspects of this technology are very well established, with cost reduction rather than technology improvement perhaps the most important issue for future development. The comparatively low melting point of gold (1064 °C, compared with 1769 °C for platinum) probably means that the material is not suitable for use in three-way catalysts that operate at the typically high temperatures (>600 °C) of stoichiometric-burn exhausts in under-floor catalyst positions, and even less so in close-coupled catalyst positions (∼1000 °C). However, low temperature start-up performance of catalysts remains an area in which improvement is sought. PGM-based TWCs lack low temperature start-up, as well as suffering prolonged idling problems, resulting in the catalyst monolith not operating until the light-off temperature (∼300 °C) required for oxidation of hydrocarbons is attained. Gold-based catalysts have the ability to be active at relatively low temperatures and can potentially be used in conjunction with the TWC in automotive catalyst systems to overcome this cold engine problem. In addition, Au-based catalysts have shown activity for the lean-burn reduction of NO_x at both high and relatively low temperatures. The patent literature indicates real industrial interest in gold in this application [12,13].

If there is found to be scope to improve the thermal durability of gold-based catalysts through inhibition of gold particle sintering, by strong interaction with transition metal oxides or even formation of stabilised ionic Au, gold catalysts could potentially be stabilised for at least application in diesel exhaust systems. Temperatures in diesel exhausts can be very low, where, for example, it is known that under a European urban driving cycle, temperatures average 80–180 °C (max. 230 °C) whilst averages of 180–230 °C (max. 440 °C) in the extra-urban part of the cycle have been observed [14]. The current research status of gold-based catalysts for automotive pollution control has been recently reviewed [12].

2.1.5. Control of other pollutants

The scientific literature is now showing that decomposition of ozone is a reaction that gold catalyses effectively [15,16]. Control of ozone, which can be emitted by equipment, such as photocopiers and laser printers, and which can be a contributor to the formation of smog, could be a potential commercial application for gold catalysts.

The treatment of gaseous emissions containing volatile organic compounds has been of increasing concern in recent years. Various options exist for removing these pollutants including thermal incineration, catalytic oxidation and adsorption. Catalytic oxidation is particularly energy efficient if the catalytic reactor can operate at lower temperatures and shorter times than thermal incineration. Gold on mixed metal oxide catalysts have been reported to show good activity in this type of reaction [5,17] for removal of undesirable pollutants, such as dioxins, and these are potential candidates for such applications.

Another possible application for gold as a catalyst is in the control of ethylene gas in storage environments. Ethylene is released into the surrounding atmosphere by plant and plant products (i.e. fruits, vegetables and floral products) during transport or storage. The overall effect is to hasten ripening, ageing and, eventually, spoilage of the perishable goods. Within the produce industry, it is estimated that losses directly related to ethene run into billions of dollars annually. The easiest way to prevent the effects of ethene on perishable crops is to remove it from the storage and handling environment. Manufacturers continue to develop new tools for removing ethene from the air, and a cheap and effective low temperature catalytic method for its control may have significant commercial potential. The investigation of gold catalysts for this application should prove to be an interesting area of research and gold is known to catalyse the hydrogenation of unsaturated hydrocarbons under mild conditions [18] and catalytic oxidation processes could also be evaluated.

2.2. Chemical processing

2.2.1. Production of vinyl chloride

One of the first practical demonstrations of the commercial relevance of catalysis by gold was by Hutchings, working then at AECI in South Africa [18,19] who demonstrated the use of gold-on-carbon catalyst for the conversion of ethyne into vinyl chloride by the addition of hydrogen chloride, a commercially important reaction for the manufacture of polyvinyl chloride:

$$HC{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$$

Gold catalysts were found to be about three times more active than the commercial mercuric chloride catalysts used at that time. One 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 three times its present value: at today's gold price, the use of gold in this process would surely be viable, especially when the recovery and recycle of the gold is taken into account. This process may yet have the potential to be applied in developing countries if market demand for PVC is sustainable.

2.2.2. Production of propene oxide

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:

$$CH_3CH{=}CH_2 + \tfrac{1}{2}O_2 \rightarrow CH_3CH(O)CH_2$$

Patents for direct propene oxide production using gold catalysts have been appearing in the literature in recent years [20,21], 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 [20], with 95% selectivity.

Haruta [22] obtained >99% selectivities at low conversions in the oxidation of propene to propene oxide using a 1 wt% Au/TiO_2 catalyst system at 50 °C, when both oxygen and hydrogen are present in the feed gas (H_2:O_2:propylene:Ar = 10:10:10:70 vol%). More recently published work has improved these results further, such that yields are at a commercially acceptable level [23]. The remaining technical challenge is the need to increase catalyst durability further, with deactivation currently occurring after a few hours on stream.

2.2.3. Direct production of hydrogen peroxide

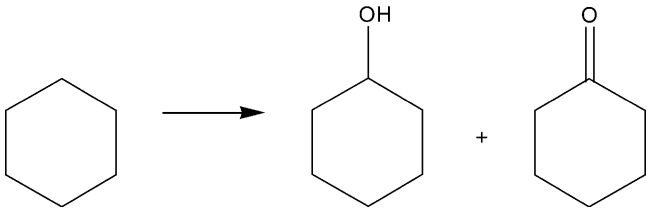
Another reaction for which gold catalysts are attracting attention is the local generation of hydrogen peroxide:

$$H_2 + O_2 \rightarrow H_2O_2$$

Global sales of hydrogen peroxide are rising at a rate of about 10% per year, due in part to it being viewed as an environmentally friendly alternative to chlorine. Currently, hydrogen peroxide is produced on a large scale (over 20,000 tonnes per annum) by the sequential hydrogenation and oxidation of an alkyl anthraquinone. Hydrogen peroxide is a hazardous material and transportation from point of manufacture to point of use is expensive and there is a definite market need to develop a safe, modular process that can be operated cost effectively at the point of use. There is evidence emerging in the literature and patent applications that gold-based catalysts might be applied effectively for this purpose [24,25]. Hutchings has reported the use of Pd/Au alloy catalysts supported on TiO_2 for this reaction [24]. By tailoring the Pd–Au ratio, very high rates of H_2O_2 can be achieved at 2 °C. This couldbe a significant application for gold-containing catalysts.

2.2.4. Production of nylon precursors

An important recent development is the demonstration that gold catalysts can be used in a solventless liquid phase system to oxidize cyclohexane to cyclohexanol and cyclohexanone using oxygen [26,27]:



Industrially, almost all the cyclohexane currently produced (4.4 million tonnes per annum and expected to grow at ca. 3%) is converted to cyclohexanol and cyclohexanone, the intermediates in the production of caprolactam and adipic acid, used in the manufacture of nylon-6 and nylon-66 polymers, respectively. 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 cyclohexanol and cyclohexanone. The large demand for these products and the high energy demands for the present process could provide a commercial driver for a more effective catalyst. The work of Zhao et al. [26] is interesting both for its comparatively high conversion rates of ca. 15% and high selectivities to cyclohexanol and cyclohexanone), with TONs of up to 3000 h^{-1}, and its use of a zeolite catalyst support. In addition, the reaction occurs in an environmentally benign oxidation protocol involving oxygen as the oxidant in a solvent-free system. The catalyst, 1% Au on ZSM-5, also seems durable, at least within the limits tried so far.

2.2.5. Hydrotreating distillates

There is continuing environmental pressure on the refining industry to progressively decrease the levels of sulfur and aromatics in gasoline and diesel distillate fuels. The present commercial dual stage system which uses a NiMo or CoMo catalyst, followed by a Pt catalyst, may not exhibit sufficient activity to achieve the final levels of sulfur and aromatics saturation required. Recent results have shown, for the first time, the possibility of using gold as a component of a hydrodesulfurization and aromatic dehydrogenation catalyst. Venezia et al. have demonstrated that Au-Pd catalysts, supported on an inert carrier, such as SiO_2, are surprisingly more active (by a factor >6) in the hydrodesulfurization of dibenzothiophene than pure palladium catalysts [28]. 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 sulfide species.

2.2.6. Selective hydrogenation

Selective hydrogenation to remove dienes and alkynes from monoolefin streams are needed to prevent poisoning of the polymerization catalysts. Supported gold catalysts offer interesting potential since they can selectively hydrogenate dienes in the presence of monoenes [29,30] and catalyse the conversion of alkynes to alkenes [31,32]. Gold could also be associated with other hydrogenation metals, such as Pt or Pd, to modify activity and/or selectivity.

2.2.7. Food processing

It has already been demonstrated by Rossi [33] that gold-on-carbon catalysts can be used very effectively to oxidize glucose to gluconic acid (an important food additive, made on the 60,000 tonnes per annum scale). It is pertinent to evaluate whether there could be further opportunities for gold in the food industry. At the 13 ICC in Paris, new results were presented relating to gold-catalysed sugar chemistry. The first by Mirescu et al. [34] reported on the selective oxidation of lactose and maltose with Au/TiO_2 catalysts, which was used to give 100% selectivity to lactobionic acid and maltobionic acid, respectively. These also 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 [35]. Earlier work by Caceres et al. reported the use of Au on SiO_2 or Al_2O_3 for the hydrogenation of canola oil [36]. It was shown that the complete reduction of linolenic acid could be achieved at a lower *trans*-isomer content in the products than that obtained using the American Oil Chemists standard nickel catalysts. Nickel catalysts have, of course, been used for over a century for the hardening of natural oils but it is possible that gold catalysts, using the much more advanced methods of preparation available today, might have a future role in this application: if so, this would have the appeal that any gold residues in the products would be completely harmless since gold is environmentally benign.

2.3. Fuel cell applications

Significant challenges must still be overcome before the widespread adoption of fuel cell technology within a new hydrogen-based economy. Amongst these challenges, the reduction in the overall cost of fuel cell systems and hydrogen infrastructure continues to be one of the most significant. The development of improved low cost catalysts that meet performance and durability requirements would undoubtedly play a major role in reducing overall cost. In a number of the catalysed reactions occurring within fuel cell systems, the current catalysts of choice are based on the use of platinum group metals. However, precious metal catalysts are a significant proportion of overall system cost and with the price of platinum currently at very high levels, effective lower cost catalysts would undoubtedly be extremely welcome.

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 [37]:

- water gas shift (WGS) for clean H_2 production;
- oxidative removal of CO from H_2 feedstocks or within the fuel cell membrane;
- the use of gold as an electrocatalyst within the fuel cell itself.

2.3.1. Water gas shift in H_2 production

One of the key issues for the fuel cell system is the small amount of CO present in the output from a fuel reformer as this can impact adversely on the performance by poisoning the Pt catalysts. The water gas shift reaction has gained new interest over recent years since it can be used to reduce the amount of CO present from the output of fuel reformers:

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

The thermodynamics of this equilibrium means that the lower the temperature used, the lower will be the proportion of carbon monoxide in the hydrogen produced with consequent reduction in the tendency for the Pt in the fuel cells to become poisoned by CO.

Catalysts for water gas shift need to achieve high conversions at comparatively low temperature, to require no special activation, and to be resistant to repeated start-up and shutdown cycles. Copper-based catalysts have traditionally been used in industry for the low temperature WGS reaction. However, these catalysts are not suitable for automotive application of fuel cells. Firstly, they are not active enough and secondly, they are pyrophoric and as a result are not suitable for repeated start-up and shutdown. This has led to renewed research into developing new catalysts that can meet these requirements. Initial research showed that gold-based catalysts are very active for the low temperature WGS reaction [38]. The early work in this area focused on Au/Fe_2O_3 catalysts [39], the activity of which was reported to exceed that of the commercial $CuO/ZnO/Al_2O_3$ low temperature WGS catalyst. Since then, a variety of different supported gold catalysts have been tested and of these catalysts, Au/Fe_2O_3 and Au/TiO_2 catalysts were found to be the most active. In addition, it was found that gold deposited on well-crystallised metal oxides exhibits higher activity than that on amorphous oxide supports. Problems with the stability of Fe_2O_3-supported catalysts and interesting results from work carried out on Pt/CeO_2 catalysts for the WGS reaction [40] has led researchers to investigate Au/CeO_2 catalysts [41]. It has been found that Au/CeO_2 catalysts are, like their Pt/CeO_2 counterparts, very active and more stable than Au/Fe_2O_3 [42].

2.3.2. Oxidative removal of CO from H_2 (PROX)

A further possible application of gold-based catalysts could be in the removal of carbon monoxide impurities from the hydrogen feedstock consumed by fuel cells (PROX). The absence of carbon monoxide from hydrogen feedstocks results in fuel cells exhibiting longer lifetimes and improved efficiency. The effectiveness of an $Au/\alpha\text{-}Fe_2O_3$ catalyst in this application has been demonstrated, exhibiting higher activity at lower temperatures than the current commercial PROX catalyst $Pt/\gamma\text{-}Al_2O_3$ [43].

In recent work by Nieuwenhuys and co-workers [44], nanoparticulate gold particles (5 nm) on mixed oxides have been shown to have superior activity for CO oxidation at low temperatures. In the $Au/MgO/MnO_x/Al_2O_3$ catalyst investigated, MgO is thought to be the stabiliser for Au particle size and MnO_x the cocatalyst. The hydrogen oxidation is relatively suppressed by the multicomponent catalyst. It is clear that interest in the use of gold catalysts for this application has not been limited to academic research, with a number of major international companies submitting patent applications in this area. These have included specific claims for the use of gold on an $MgAl_2O_4$ spinel catalyst, an Au/Ru alloy catalyst and an Au/Fe_2O_3 catalyst for removal of CO down to <1% [45–47]. This appears to be a promising commercial application area.

2.3.3. Gold as an electrocatalyst

The application of gold as an electrocatalytic component within the actual fuel cell has to date been limited primarily to the historical use of an Au-Pt bi-metallic electrocatalyst for oxygen reduction in the Space Shuttle/Orbiter alkaline fuel cells (AFC) [48] and the recently claimed use of gold for borohydride oxidation in the direct borohydride alkaline fuel cell (DBFC) [49,50]. Electrocatalysts with lower cost, improved CO tolerance and higher performance are needed for the membrane/electrode assemblies of other low temperature fuel cells (PEMFC and DMFC). 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 bi-metallic system with platinum group metals [51–53].

Recent results on gold and gold–platinum alloy nanoparticles as potential fuel cell electrocatalysts are encouraging [51,54,55]. This work has focused on refining the synthesis, assembly and thermal treatment of shell-capped Au and AuPt nanoparticles in the 2–5 nm size range and comparing the electrocatalytic oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) activities of the Au and AuPt nanoparticle catalysts with commercially available Pt/C and PtRu/C catalysts. The AuPt catalysts with >70% Au and 10–25% metal loading exhibited at least comparable, and in some cases much higher catalytic activities than Pt (ORR) and PtRu catalysts (MOR) in alkaline electrolytes.

3. Other relevant issues

3.1. Precious metal costs and availability

Whilst the cost of a material used as a catalyst is a consideration for some industrial end-users, the most important motivating factor for new catalyst development from a chemical companies 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. This reflects their often increased activity and durability in many reactions compared to alternative base metal catalyst systems, and of course, precious metals are economically recycled.

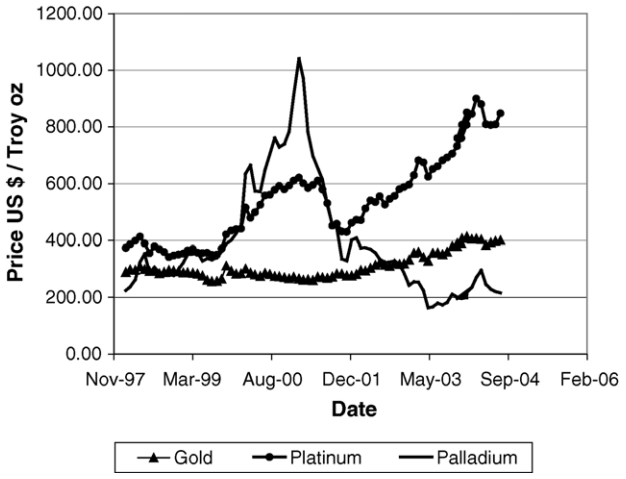


Fig. 1. Precious metals prices 1998–2004.

However, catalyst cost and availability is 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 (Fig. 1) 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 like the fuel cell industry.

3.2. Gold reference catalysts

At the 'Catalytic Gold' International Conference in Cape Town in 2001 [56,57], it was suggested that a gold reference catalyst or catalysts should be made widely available to researchers to enable them to benchmark their own research and enable comparison with the work of other laboratories. In much the same way, platinum-based reference catalysts were made available in the 1970s (and indeed still are). Based on this suggestion, World Gold Council commissioned a range of gold reference catalysts from Sud Chemie in Japan in 2002, under the guidance of AIST, Japan's National Institute of Advanced Science and Technology [58]. The availability of the reference catalysts enables researchers to compare their own experimental results with those of other groups and it is believed that this supports the

Table 1
Details of the Reference Catalyst Programme

Catalyst type	Method
(A) 1.5 wt% Au/TiO_2 (P25)	Deposition/precipitation
(B) 0.3 wt% Au/Fe_2O_3 on alumina beads	Deposition/precipitation
(C) 4.5 wt% Au/Fe_2O_3	Coprecipitation
(D) 0.8 wt% Au/C (Cabot XC72)	Gold sol
Other details	
Size of each batch	5 kg
Calcination conditions (for A–C)	573 K
Storage conditions	Room temperature in glass
Manufacturers	Süd Chemie (A–C), University Milan (D)
Distribution	World Gold Council

development and application of gold catalysts. A fourth reference catalyst (1% Au on carbon) is also available, having been prepared by Prof Michele Rossi of the University of Milan (Table 1). Over 120 samples of reference catalyst have so far been supplied to universities and industrial companies and up to date information on the catalysts and their availability can be obtained from World Gold Council. Recipients of these catalysts are encouraged to share their results both in the characterization and activity spheres.

3.3. Catalyst preparation methods and availability of precursors

Many researchers in applied gold catalysis hope ultimately to observe the results of their work being used in useful practical applications, to the benefit of industry and society. Unfortunately, some currently studied methods for preparing gold catalysts are unlikely to be scaleable for commercial applications. A financially viable catalyst preparation process should be based on the complete removal of precious metal from the liquid phase and some techniques fail in this regard. Deposition precipitation techniques, whilst producing highly active catalysts, also consume large quantities of water and the cost of treatment of wastewater is an expensive additional process step. Other preparation methods, such as appropriate modifications of impregnation via incipient wetness techniques, are more likely to be suitable for commercial production if they lead to reproducible, stable and active catalysts and reduce the resulting quantities of wastewater. This should be an important consideration for researchers working in applied fields. The commercial exploitation of gold catalysts on a significant scale awaits the development of such processes and availability. This is potentially a limiting factor in the exploitation of gold catalysts.

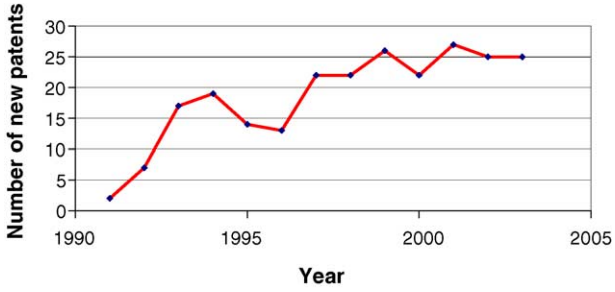


Fig. 2. Number of patents based on catalysis by gold (1991–2003).

3.4. Patents

Patent applications are a useful indication of industrial interest in a particular area of technology and it is therefore instructive to review the patent literature on gold catalysis to understand which industries and companies appear to have a genuine interest in their industrial use. It is clear, that broad industrial interest in gold appears to have been increasing since the early nineties (Fig. 2). It is particularly interesting to note the large number of major companies who have applied for patents on gold catalyst technology (Table 2).

Many of these are major multinationals with a history of innovation and new technology development. It is considered their interest in gold-based catalysts is genuine, with several companies believed to have pilot plants in operation.

Table 2
Examples of patent applications in the area of gold catalysis

Application area	Use	Example patent application	Company
Pollution control	Odour abatement	JP 05131139	Matsushita Electric Ind.
	NO_x removal	JP 06039284	Mitsui Kozan
	Mercury emission control	US 6136281	Tennessee Valley Authority
	Room air purification	JP 04371228	AIST Japan
	Automotive emission control	JP 10216518	Toyota Jidosha
Chemical processing	Production of vinyl acetate monomer	EP 0654301	BP Chemicals
	Direct formation of hydrogen peroxide	WO 02/064500	Arco Chemical Technology
	Production of propylene oxide	US 2003/0060643	Bayer Corp.
Hydrogen economy	Water gas shift catalyst	DE 10205873	ZSW, Germany
	Hydrogen purification—PROX	EP 1209121	Haldor Topsoe
	Fuel cell electrocatalyst	JP 2002305001	Matsushita Electric Ind.

4. Conclusions

This paper has summarised the major commercial opportunities to apply heterogeneous gold catalysis and has highlighted those areas that are considered by the authors to merit particular attention. However, it is not and cannot be an exhaustive list of possible application areas, since new reactions that are catalysed by gold continue to be discovered on an on-going basis. Overall, it is believed that there is cause for great optimism that many new applications for gold catalysis could emerge over the next decade. To turn this expectation into reality requires researchers to be proactive in exploiting promising research results and effectively communicating these to industry. In addition, potential end-user industries and catalyst manufacturers need to carefully and fully consider the potential business opportunities that gold-based catalysts undoubtedly offer. The series of recent international gold catalysis conferences are proving to be a key forum for encouraging exploitation in this regard [56,57,59], enabling an exchange of ideas and opportunities between industry and academia. Indeed, as was emphasized at the most recent of these events, GOLD 2003, all involved in this exciting field need to carefully consider both the durability of catalysts under representative operating conditions and commercially viable methods of catalyst preparation, which potentially limit the practical application of this exciting science that has developed in recent years.

References

[1] G.J. Hutchings, J. Catal. 96 (1985) 292.
[2] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. 4 (1987) 405.
[3] W.D. Provine, P.L. Mills, J.J. Lerou, Stud. Surf. Sci. Catal. 101 (1996) 191.
[4] Process for the preparation of catalysts for use in the production of vinyl acetate, European Patent Application EP 0654301, BP Chemicals, 1994.
[5] M. Haruta, CATTECH 6 (2002) 102.
[6] S.A.C. Carabineiro, D.T. Thompson, Catalytic applications for gold nanotechnology, in: Nanocatalysis: Principles, Methods and Case Studies, Springer-Verlag, 2005.
[7] Gold catalyst for removal of nitrogen oxide and method for removing nitrogen oxide, Japanese Patent Application JP 4281846, AIST, 1992.
[8] Control of malodor, Japanese Patent Application JP 5115748, Matsushita Electric Ind., 1993.
[9] F. Luck, Catal. Today 53 (1999) 81.
[10] M. Besson, A. Kallel, P. Gallezot, R. Zanella, C. Louis, Catal. Commun. 4 (2003) 471.
[11] S. Meischen, in: Proceedings of the GOLD 2003, Vancouver, Canada, September–October, 2003.
[12] G. Pattrick, E. van der Lingen, C.W. Corti, R.J. Holliday, D.T. Thompson, Top. Catal. 30–31 (2004) 273.
[13] Catalyst for purifying an exhaust gas, European Patent EP 1043059 A1, Toyota Jidosha, 2000.
[14] K.M. Adams, J.V. Cavataio, R.H. Hammerle, Appl. Catal. B: Environ. 10 (1996) 157.
[15] Z. Hao, D. Cheng, Y. Guo, Y. Liang, Appl. Catal. B: Environ. 33 (2001) 217.
[16] P.M. Konova, A.I. Naydenov, D.R. Mehandjiev, Bulgarian Chem. Commun. 34 (2002) 437.
[17] O. Kajikawa, X.-S. Wang, T. Tabata, O. Okada, Organohalogen Compd. 40 (1999) 581.
[18] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.
[19] G.J. Hutchings, Gold Bull. 29 (1996) 123.
[20] Epoxidation of olefins using molecular oxygen and hydrogen involves catalyst comprising gold on support material, Patent Application WO 200158887, Bayer AG, 2001.
[21] Catalyst for the production of epoxide comprises carrier containing oxide of titanium and/or zirconium, and gold fine particles fixed on the carrier, Patent Application US 2001020105, Nippon Shokubai, 2001.
[22] M. Haruta, Catal. Today 36 (1997) 153.
[23] M. Haruta, in: Proceedings of the GOLD 2003, Vancouver, Canada, September–October, 2003.
[24] P. Landon, P.J. Collier, A.J. Papworth, C.J. Kiely, G.J. Hutchings, Chem. Commun. (2002) 2058.
[25] Process for producing hydrogen peroxide, Patent Application WO 02064500, Arco, 2002.
[26] R. Zhao, D. Ji, G. Lv, G. Qian, L. Yan, X. Wang, J. Suo, Chem. Commun. (2004) 904.
[27] Gold-zeolitic oxidation catalysts for the conversion of cyclohexane into cyclohexanone and cyclohexanol, US Patent 2004258103 A1, August, 2004.
[28] A.M. Venezia, V. La Parola, V. Nicolì, G. Deganello, J. Catal. 212 (2002) 56–62.
[29] D.A. Buchanan, G. Webb, J. Chem. Soc., Faraday Trans. 71 (1975) 134.
[30] M. Okumura, T. Akita, M. Haruta, Catal. Today 74 (2002) 265.
[31] P.A. Sermon, G.C. Bond, P.B. Wells, J. Chem. Soc., Faraday Trans. 75 (1979) 385.
[32] J. Jia, K. Haraki, J.N. Kondo, K. Tamaru, J. Phys. Chem. B 104 (2000) 11153.
[33] M. Rossi, in: Proceedings of the GOLD 2003, Vancouver, Canada, September–October, 2003.
[34] A. Mirescu, U. Pruesse, K.-D. Vorlop, in: Proceedings of the 13th International Congress on Catalysis, Paris, France, July, 2004, P5-059.
[35] S. Schimpf, B. Kusserow, Y. Önal, P. Claus, in: Proceedings of the 13th International Congress on Catalysis, Paris, France, July, 2004, P5-060.
[36] L. Caceres, L.L. Diosady, W.F. Graydon, L.J. Rubin, J. Am. Oil Chem. Soc. 62 (1985) 906.
[37] D. Cameron, R. Holliday, D. Thompson, J. Power Sources 118 (2003) 298.
[38] D. Andreeva, Gold Bull. 35 (2002) 82, and references therein.
[39] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, J. Catal. 158 (1996) 354.
[40] H. Cordatos, T. Bunluesin, J.S. Stubenrauch, J.M. Vohs, R.J. Gorte, J. Phys. Chem. 100 (1996) 785.
[41] Q. Fu, A. Weber, M. Flytzani-Stephanopolous, Catal. Lett. 77 (2001) 87.
[42] J.J. Baschuk, X. Li, Int. J. Energy Res. 25 (2001) 695.
[43] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 182 (1999) 182, 430.
[44] R. Grisel, K.-J. Westgate, A. Gluhoi, B.E. Nieuwenhuys, Gold Bull. 35 (2002) 39.
[45] Process for the catalytic oxidation of carbon monoxide and/or methanol, European Patent Application EP 1209121, Haldor Topsoe, 2002.
[46] Catalyst and process for removing carbon monoxide from a reformate gas, US Patent Application US 20030012719, OMG AG, 2002.
[47] Production of Hydrogen Containing Gas, Japanese Patent JP 2153801, Mitsubishi, 1990.
[48] J.O'M. Bockris, A.J. Appleby, Assessment of research needs for advanced fuel cells, in: S. Penner (Ed.), Energy, vol. 11, No. 1–2, 1986, p. 110 (Chapter 3).
[49] R.W. Reeve, I.E. Eweka, G.O. Mepsted, Eighth Grove Fuel Cell Symposium, London, September 24–26, 2003, 04B.6.

[50] J.B. Lakeman, K. Scott, Abstract, Conference on High Energy Density Electrochemical Power Sources, Nice, France, September 17–20, 2003.
[51] (a) C.J. Zhong, M.M. Maye, Adv. Mater. 13 (2001) 1507;
(b) C.J. Zhong, J. Luo, M.M. Maye, L. Han, N.N. Kariuki, Nanostructured Gold and Alloy Electrocatalysts, in: B. Zhou, S. Hermans, G.A. Somorjai (Eds.), Nanotechnology in Catalysis, Kluwer Academic/Plenum Publishers, 2003 (Chapter 11).
[52] Electrode catalyst for fuel cells, Japanese Patent Application JP 305001, Matsushita Electric Ind. Co., 2002.
[53] K. Matsuoka, Y. Iriyama, T. Abe, Z. Ogumi, 2004 ECS Joint International Meeting, Tapa, October 3–8, 2004 (Abstract 1518).
[54] M.M. Maye, J. Luo, L. Han, N.L. Kariuki, C.-J. Zhong, Gold Bull. 36 (2003) 75.
[55] C.-J. Zhong, J. Luo, M.M. Maye, L. Han, N. Kariuki, Proceeding of the GOLD 2003, Vancouver, Canada, September–October, 2003.
[56] Catalytic Gold 2001, Catal. Today 72 (1–2).
[57] D.T. Thompson, Gold Bull. 34 (2001) 56.
[58] http://www.gold.org/discover/sci_indu/gold_catalysts/refcat.html.
[59] GOLD 2003 Keynote Papers, Gold Bull. 37 (2004) 1–2.