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Gold's future role in fuel cell systems

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Abstract

Innovative recent research has suggested that gold-based catalysts are potentially capable of being effectively employed in fuel cells and related hydrogen fuel processing. The justification for developing the gold catalyst technologies described, is not only based on their promising technical performance, but also the relatively low stable price and greater availability of gold compared with the platinum group metals. The employment of gold catalysts could therefore produce a welcome reduction in the capital cost of fuel cell installations. The most likely first use for gold catalysts is for the removal of carbon monoxide impurities from the hydrogen feedstock streams used for fuel cells. Such hydrogen is usually obtained from reforming reactions (from hydrocarbons or methanol) either from free-standing plant or from an onboard reformer in a vehicle in the case of transport applications. Absence of carbon monoxide would enable fuel cells to run at lower temperatures and with improved efficiency. Effectiveness of gold catalysts in this application has already been demonstrated. Preferential oxidation (PROX) of carbon monoxide in hydrogen-rich reformer gas is best effected by a gold catalyst (Au/α -Fe₂O₃) which is significantly more active at lower temperatures than the commercial PROX catalyst, i.e. Pt/γ -Al₂O₃ currently used for this purpose. Supported gold catalysts are also very active in the water gas shift reaction used for producing hydrogen from carbon monoxide and water. Research has shown that gold supported on iron oxide (Au/ α -Fe₂O₃) catalyst is more active at lower temperatures than both the α -Fe₂O₃ support and the mixed copper/zinc oxide (CuO/ZnO) catalyst currently used commercially. Preparation of gold on iron oxide and gold on titania (Au/Fe₂O₃ and Au/TiO₂) by deposition–precipitation produces more active catalysts than by conventional co-precipitation. Other applications for gold in fuel cells are described and include its use as a corrosion resistant material and the incorporation of gold catalysts to provide useful improvements in electrode conductivity.

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1. Introduction

In many of the catalysed reactions in fuel cell technology, the current catalyst of choice is based on the use of platinum group metals (PGMs). One of the current barriers to commercialisation of fuel cells, is the technology advance required to decrease precious metal contents in catalysts and yet still achieve the required power output (i.e. a reduction in the US\$/kW price equation). Based on the achievement of acceptable technical performance, the use of gold in preference to platinum (or other PGMs) could help to reduce the cost of fuel cell technology.

It can be seen, Fig. 1, that since 1998 the price of platinum and palladium has exceeded that of gold. In addition, the gold price has been characterised by a remarkably stable value compared to the widely fluctuating prices of the PGMs [1,2].

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A discussion centred on the exact reasons for metal price fluctuations and trends is outside the scope of this paper, but the relatively greater availability of gold compared to the PGMs is undoubtedly important in explaining the comparative stability of the price of gold in recent years, Fig. 2.

It is certainly true that concerns over platinum group metal supply in recent years have led to some issues arising with regard to the cost of these metals. Since the 1970s national governments have gradually imposed increasingly stringent emissions regulations on the automotive industry, with the result being that today's vehicles emit far lower levels of pollutants than previously. The success of the platinum group metals in helping manufacturers produce successive, improved generations of automotive catalysts which have met these pollution control targets is undeniable. The importance of these metals can be seen in the steady rise in their consumption in such applications, over the last two decades (Fig. 3).

Should the commercialisation of fuel cell powered vehicles take place in the next decade as is promised, the

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Fig. 1. Variations in PGM and gold prices since 1996 [1,2].

adequate cost effective supply of PGMs may prove to be an issue in the long term. It is also probably reasonable to assume that large scale implementation of fuel cell technology will not be possible without PGM recovery. The comparatively large holdings of gold in the world would be a benefit, in that wide scale use as a catalyst in any one application will be unlikely to produce unpredictable fluctuations in price, and this would favour its use compared to the platinum group metals.

Clearly then, with the ever present focus on long term cost competitiveness, a comparatively cost effective precious metal for catalytic applications is potentially very attractive for the fuel cell industry.

2. Current understanding of gold catalysis

Gold catalysis is a rapidly developing topic of both academic and industrial research and significant advances have been made within the last decade [4–11]. In particular, it is interesting to note the increasing number of patents related to gold catalysts in polymer electrolyte membrane (PEM) fuel cell technology, including some from major original equipment manufacturers [12,13]. However, compared to research focused on the PGMs, the science of gold catalysis is still quite new, and is underdeveloped. Nonetheless, it has already been demonstrated that gold can have the highest catalyst activity for some reactions, including the



Fig. 3. Consumption of PGMs in automotive catalysts since 1983 [1,2].

oxidation of carbon monoxide and the hydrochlorination of ethyne and it is believed that in a number of specific areas, gold catalysts will be used in commercial applications, including pollution control. The reactions for which gold has already been demonstrated to be a strong catalyst include:

- oxidation of CO and hydrocarbons,
- water gas shift (WGS),
- reduction of NO with propene, CO or H₂,
- reactions with halogenated compounds,
- water or H_2O_2 production from H_2 and O_2 ,
- removal of CO from hydrogen streams,
- hydrochlorination of ethyne,
- selective oxidation, e.g. epoxidation of olefins,
- selective hydrogenation,
- hydrogenation of CO and CO₂.

3. Reactions relevant to fuel cells

3.1. Hydrogen purification—preferential oxidation of carbon monoxide

The most likely first use for gold catalysts in fuel cell systems is for the removal of carbon monoxide impurities from the hydrogen streams used for fuel cells. This hydrogen is usually obtained from reforming reactions



Fig. 2. Gold and PGM mine production for the year 2000 [2,3].

(from hydrocarbons or methanol), either from free-standing plant or from an on-board reformer.

In low temperature fuel cells such as PEM types, carbon monoxide is preferentially absorbed, leading to rapid deterioration in performance. It is common practice to add a small percentage of oxygen (1-2%) to the contaminated hydrogen fuel stream and pass it over a catalyst bed to oxidise the carbon monoxide to the less harmful carbon dioxide upstream of the fuel cell stacks. Higher temperature fuel cells such as phosphoric acid types must be operated at a sufficiently high temperature (around 473 K) to prevent the carbon monoxide being strongly absorbed at the anodes.

Improved removal of carbon monoxide from the fuel stream would enable low temperature fuel cells to run at higher efficiency and with lower anode catalyst loadings, and intermediate temperatures fuel cells to operate at somewhat reduced temperature with resulting improvements in durability.

Preferential oxidation of carbon monoxide (PROX) in hydrogen-rich reformer gas is effected by a gold catalyst (Au/ α -Fe₂O₃) which is significantly more active than the commercial PROX catalyst, i.e. Pt/ γ -Al₂O₃ used for this purpose [14]. As mentioned above, the hydrogen/oxygen reaction which is also used in fuel cells is also catalysed by gold but at higher temperatures than the oxidation of carbon monoxide [9].

It has been shown [15] that Au/CeO₂ and Au/ α -Fe₂O₃ catalysts, made using a deposition precipitation technique, are effective in selective carbon monoxide oxidation (SCO) in hydrogen-rich gas. The deactivation of the latter catalyst can easily be reversed. Using a range of support oxides, it was shown that the individual CO and H₂ oxidation reactions are affected to a different extent by the choice of support oxide. The variations in long-term stability are related to the different tendencies of the various support oxides to form surface carbonates which impair both the CO and H₂ oxidation reactions: magnesia- and Co3O4-supported catalysts are the most strongly affected in this way. The Au/ α -Fe₂O₃ catalyst is the most active catalyst tried to date and complete reversibility of the deactivation can be achieved using simple flushing of the catalyst bed with an inert gas, suggesting the use of flushing cycles for practical applications. There is also evidence that the ratio between the gold and support oxide particle sizes has an influence on performance.

Recent work by Nieuwenhuys and co-workers [16] has shown that nanoparticulate gold particles (5 nm) on mixed oxides have superior activity for CO oxidation at low temperatures (see Table 1). In the Au/MgO/MnO_x/Al₂O₃ catalyst, MgO is thought to be stabiliser for Au particle size, and MnO_x the co-catalyst. The hydrogen oxidation is relatively suppressed by the multicomponent catalyst.

Kung and co-workers [17] have pointed out that following Haruta's demonstration that gold supported on transition metal oxides is very active for CO oxidation, it has been

Table 1

Carbon monoxide and hydrogen oxidation over alumina supported gold catalysts (gold loading: 5 wt.%)

Catalyst	Average Au particle size (nm)	CO oxidation		H ₂ oxidation	
		α(CO)	<i>T</i> _{50%} (°C)	$\alpha(H_2)$	$T_{25\%}$ (°C)
Au	3.6 ± 1.4	0.22	57	0.16	63
Au/MnO_x	9.2 ± 2.7	0.49	35	0.19	102
Au/MgO	2.2 ± 1.0	0.59	<20	0.41	<20
Au/MgO/MnO _x	2.7 ± 1.0	1.00	<20	0.19	57

Conversion α at 20 °C and temperature needed for a conversion of 25% hydrogen and 50% (CO). Ratio CO/O₂ = 1 and H₂/O₂ = 4. Reactant flow 40 ml/min, GHSV = 2500 h⁻¹ with a mixture of H₂, CO and O₂ in helium (96 vol.%).

observed that Au/γ -Al₂O₃ is active for SCO in hydrogen. These two reactions differ in that while the CO conversion activity is stable in SCO, it declines rapidly with time on stream in CO oxidation. Thus, the presence of hydrogen during SCO successfully prevented deactivation. It was also found that Au/γ-Al₂O₃ catalyst deactivated in the course of CO oxidation could be effectively regenerated by exposure to hydrogen at room temperature. The extent of regeneration, however, depended on the partial pressure of hydrogen, the duration of hydrogen treatment and the history of the sample. The activity could be fully restored by flowing the SCO feed over the catalyst. Regeneration could also be achieved by flowing He containing 1.8% water vapour. Conversely, significant loss in CO conversion was observed when Au/ γ -Al₂O₃ catalyst was heated to 100 °C or higher in dry He, O₂ or H₂. Again, such a thermally deactivated catalyst can be fully regenerated by a short exposure to the SCO feed.

These results suggest that the active sites contain hydroxyl groups, which could be removed by de-hydroxylation or by CO oxidation. The mild temperature needed for the dehydroxylation suggests that the hydroxyl groups are associated with Au. These hydroxyl groups participate in the reaction possibly by reaction with CO to form an active intermediate in the CO₂ production pathway. Deactivation during CO oxidation is due to the depletion of the hydroxylated active sites when the reaction intermediate transforms into a stable surface species. These surface species, possibly surface carbonate, can be removed by reaction with hydrogen to regenerate the hydroxyl groups. The effectiveness of the SCO feed in regeneration is because hydrogen can be oxidised to water and react with the stable surface species that poison the active site. Consistent with the interpretation that an hydroxylated species is part of the active site is the high susceptibility of these catalysts to poisoning by chloride ions, since the chloride may displace the OH groups.

Dr. Haruta's group at AIST filed a patent on this application [18]. Fine grained gold particles on oxide supports such as MnO, CuO, ZnO, SnO₂, TiO₂ and NiO were found to be suitable for gases obtained from air or steam reforming of



Fig. 4. Temperature dependence of the catalytic activity of supported gold and base metal oxide catalysts in the water gas shift. Starting reaction gas mixture was 4.88 vol.% carbon monoxide in argon; water vapour partial pressure 223 Torr; SV 4000 h⁻¹; 1 atm. Au/ α -Fe₂O₃ (\bigcirc); CuO/ZnO/Al₂O₃ (\square); α -Fe₂O₃ (\bigcirc); Au/Al₂O₃ (\blacksquare). Rates are expressed in mol/m² h × 10⁻².

hydrocarbons such as methane and methanol. This followed a Mitsubishi patent [19] claiming the use of Au/Fe₂O₃ for removal of CO down to <1%. Patent activity from the other research groups is also expected.

The incorporation of gold catalysts into the anode gas diffusion layer of PEM cells could reduce the CO content and increase the cell efficiency.

3.2. Clean hydrogen production-water gas shift reaction

Hydrogen for fuel cells is generally produced from an organic fuel such as methanol or natural gas, using a steam reformer, followed by the water gas shift (WGS) reaction, e.g.

$$\begin{array}{l} CH_4 + H_2O \rightarrow 3H_2 + CO \\ CO + H_2O \rightarrow H_2 + CO_2 \quad (WGS) \end{array}$$

The results obtained from the use of Au/ α -Fe₂O₃ and Au/ Al₂O₃ in the catalysis of the water gas shift are given in Fig. 4; the catalysts were prepared by co-precipitation and characterised using X-ray diffraction (XRD) and transmission electron microscopy (TEM) [20–22]. It is clear that the Au/ α -Fe₂O₃ catalyst is more active at lower temperatures than both the α -Fe₂O₃ support and the CuO/ZnO catalyst currently used commercially; but Au/Al₂O₃ prepared by co-precipitation has a very low activity. Preparation of Au/Fe₂O₃ [23] and Au/TiO₂ [24] deposition–precipitation produces more active catalysts than by co-precipitation.

Both Au/ α -Fe₂O₃ and Au/TiO₂ catalysts are active at low temperatures for the WGS reaction. For the forward reaction, the rate at 373 K increased with increasing gold loading for a series of Au/TiO₂ catalysts prepared by deposition– precipitation. Au/TiO₂ prepared by co-precipitation gave a lower rate despite higher metal loading and the smallest gold particle sizes. Au/Ni(OH)₂ is also active in the WGS reaction; the co-precipitated catalyst was demonstrated to be more active than Ni(OH)₂ itself over the temperature range 433–633 K. In a more recent paper [25], reporting a comparative study on Au/Fe₂O₃, Au/Co₃O₄, and Au/TiO₂, it was established that Au/TiO₂ was the most active catalyst, confirming the superiority of TiO_2 over α -Fe₂O₃ found earlier by Haruta et al. In the iron oxide supported catalyst used for the work illustrated in Fig. 4, the gold particles had an average size of 3.5 nm and were situated in close proximity to the iron oxide crystallites. In the more recent work the particle sizes for the α -Fe₂O₃-supported catalysts prepared by co-precipitation and deposition-precipitation were both ca. 2 nm. In the Ni(OH)₂ catalyst described above the particle size was ca. 8-10 nm, and in the results obtained by Haruta, the particle size was within the range 2.8–4.9 nm depending on method of preparation using various supports. These particle sizes are similar to those in the catalysts used effectively for the hydrogenation of carbon oxides to methanol and for the carbon monoxide oxidation reaction; similar considerations of increase in specific activity for gold as the particle size decreases seem to apply in all these reactions.Andreeva et al. [26] have proposed a mechanism involving dissociative adsorption of water on small gold particles. followed by a spillover of activated hydroxyl groups onto adjacent sites of the ferric oxide. If this mechanism is correct, then the presence of a high surface hydroxyl coverage on magnetite should characterise the working catalyst, but the adsorption of carbon monoxide is not described and how the reaction with carbon monoxide occurs is not defined. TPR has shown that the hematite/magnetite transition in Au/ α -Fe₂O₃ takes place at about 140 K lower temperature than in α -Fe₂O₃. Consequently, in the presence of gold the most advantageous working structure of the catalyst is attained at a significantly lower temperature, and this explains the increased low temperature activity of the supported gold catalyst compared with that for the support alone.

At the 2001 conference on 'Catalytic Gold' in Cape Town [27], the activities of Au/CeO_2 catalysts for the WGS reaction were reported for the first time. These results are of particular interest since ceria (CeO₂) has been shown to be a crucial component of emission-control catalysts, principally because of its role in oxygen storage. A series of three samples of Au/CeO₂ were studied with different gold contents (1, 3 and 5 wt.% Au). The deposition-precipitation method was used to deposit gold hydroxide on suspended ceria in water. The XRD data analysis of the samples indicated that in the 5 wt.% Au sample the average size of gold particles was about 4-5 nm. The catalytic activity of the samples was evaluated for WGS activity over a wide temperature range (120-360 °C). The addition of gold leads to a considerable increase of the activity and stability of the catalysts.

3.3. Other potential applications for gold in fuel cells

As well as the application of gold in fuel processing, the beneficial properties of gold could produce improvements in fuel cell conductivity and activity. Even though they have been used for many years in specialised low temperature alkaline electrolyte fuel cells, gold catalysts have not been widely investigated, and in particular, the electrocatalytic properties of highly dispersed small particles are largely unexplored. As well as forming alloys with the platinum group metals, there is evidence that pure gold has electrocatalytic activity in a wide range of electrochemical oxidation reactions of organic species, in acid as well as alkaline media [28].

The use of Au/Pt alloy catalyst systems has been patented [29], and platinum/gold cathode catalysts used in the alkaline electrolyte fuel cells for the space shuttle programme.

Polymer electrolyte membrane fuel cells are dependent on extremely thin catalyst layers bonded to the electrolyte. The electrolyte becomes very acidic and corrosive during operation, since it is highly charged with protons, and any material used in conjunction with the catalyst must be highly corrosion resistant, as well as exhibiting good electrical conductivity. In order to minimise the thickness of the catalytic reaction zone, early PEM fuel cells used pure, high surface area platinum blacks. In order to improve precious metal utilisation and reduce costs, later versions incorporate platinum or platinum/ base metal alloys dispersed on carbon catalysts.

However, in attempts to reduce the thickness of the reaction layer, progressively higher metal loadings on carbons have been used, increasing from 10% to upwards of 50% and even 70% platinum by weight of catalyst. Unfortunately, as successively higher metal loadings on carbon substrate are achieved, there is a tendency for the platinum particle size to increase, and for the surface area and activity per gram of precious metal to decrease. Bearing in mind that the theoretical dispersion of a platinum catalysts is around 200 m²/g, a platinum on carbon catalyst with perhaps 40 m²/g has most of the active metal sub-surface and therefore inaccessible to the reactants.

As operating current densities tend to increase with time, there is a considerable incentive to use support materials with improved conductivity. As shown in Table 2, gold has considerably better electrical conductivity than platinum, and much better than the average carbon $(0.057 \ \mu\Omega)$.

The incorporation of a proportion of gold rather than carbon into these catalysts could therefore improve the electrical conductivity of the resulting catalytic layers, and also improve the gas accessibility of the active sites by creating a thinner layer.

Molten carbonate fuel cells (MCFCs) use electrolytes consisting of eutectic mixtures of lithium and potassium carbonates at temperatures of around 600–650 $^{\circ}$ C, which

Table 2 Properties of gold and platinum

Property	Gold	Platinum	
Conductivity $(\mu\Omega)$	0.71	0.17	
Density (g/cm ³)	19.3	21.4	
Melting point (°C)	1063	1769	

Table 3Corrosion test results on metals

Material	Test duration (h)	Initial weight (g)	Weight change (%)	Weight change (g)
Rhodium	93.6	0.604	0.33	-0.002
Ruthenium	93.6	0.940	0.21	+0.002
Platinum	93.1	0.369	0.54	+0.002
Palladium	93.1	0.816	0.49	+0.004
Gold	90.2	2.060	0.00	0.000
Silver	93.6	1.760	0.08	+0.001
Stainless steel (321-type)	90.1	0.419	2.10	+0.009
Stainless steel (304-type)	90.1	0.921	1.80	+0.017

Li_2CO_3:K_2CO_3 = 62:38 mol%: under 68% H_2, 17% CO_2, 15% H_2O at 650 $^\circ\text{C}.$

imposes considerable demands on the materials of construction. This has considerably delayed the development of the technology, although lifetimes of upwards of 10,000 h are now reported for MCFCs. Specific areas requiring gas and electrolyte seals, as well as improved electrical contact, could benefit from the use of gold since it is the only material shown to be immune to corrosion from the molten electrolyte.

Corrosion test results obtained by Wyatt and Fisher [30] are shown in Table 3. From these, it is evident that gold was not affected by immersion in molten carbonate electrolytes over periods exceeding 90 h. Indeed, gold crucibles were used to contain the molten carbonate electrolyte for much of the work. Hence, it is considered possible that many components exposed to the elevated temperatures and highly corrosive conditions experienced in solid oxide fuel cells could benefit from the use of gold/gold alloys.

4. Remaining technical barriers

There is now sufficient information to be sure that supported gold nanoparticles form the basis for catalyst systems with commercial potential for application in the generation and purification of hydrogen streams for fuel cells. The use of gold and gold alloy catalysts in the fuel cells themselves may also prove to be technically and economically attractive. However, further optimisation studies are required to establish greater reproducibility with respect to catalyst preparation, and to determine stability in terms of sintering and poison resistance during use. Ways are foreseen for overcoming these problems. Catalysts for the removal of CO from hydrogen can be regenerated using treatment with inert gases. At the low temperatures that gold catalysts are typically active, sintering is unlikely to be a problem, but ways of stabilising them at the higher temperatures likely to be required in some applications: this is an area which needs more exploration.

Consequently, two programmes of work have just begun to answer these questions and improve the overall understanding of the science.

5. Reference gold catalysts

At the first major international conference of gold catalysis, 'Catalytic Gold 2001', held in Cape Town in April 2001, it was suggested that 'reference' gold catalysts should be made available to researchers in this field for comparison purposes [31]. The World Gold Council is therefore sponsoring the preparation of the following catalysts in collaboration with Dr. Haruta (Research Institute for Green Technology, AIST, Tsukuba, Japan), Professor Michele Rossi (University of Milan) and Professor Geoffrey Bond:

- 1. 0.3 wt.% Au/Fe₂O₃/Al₂O₃ as beads by deposition precipitation;
- 2. 3 wt.% Au/TiO₂ (P-25) as powder by depositionprecipitation;
- 3. 5 wt.% Au/Fe₂O₃ as powder by co-precipitation;
- 4. 10 wt.% Au/C (Cabot XC72R) as powder using gold sol.

Catalysts 1–3 are being characterised with respect to gold loading, gold particle size, gold dispersion and catalytic activity in CO oxidation and hydrogen oxidation. Their activity will also be assessed in relation to the catalysts described above for use in the reactions useful for fuel cell technologies.

Appropriate characterisation and reactivity data will also be provided for the gold on carbon catalyst which is to be assessed for use in fuel cell applications as well as liquid phase chemical reactions.

6. EU network project: Auricat

This is a new project starting in September 2002 with a budget of \in 1,493,075 spread over 4 years, involving eight European universities and four major industrial companies together with the World Gold Council. The work will involve a detailed and systematic study of gold as a catalyst for a number of commercially important reactions, principally oxidations and hydrogenations, including reactions relevant to fuel cell technology. Studies will include improvements in the methods currently available for catalyst preparation, catalyst stability during use, and detailed mechanism elucidation. New catalysts will also be prepared and selected catalysts evaluated in existing and new reactions. Catalyst characterisation studies will be undertaken before, during and after use.

7. Conclusions

Gold catalysis is still at an early stage of development but enough is already known to be aware of its exciting potential for use in fuel cells. Further work is ongoing in many academic and industrial laboratories which will define the extent to which this potential may be realised in the future. Practical applications for gold catalysts will naturally require reliable methods of manufacture and a secure knowledge of their long-term mechanical and catalytic stability as well as their performance criteria, including activity and durability under practical operating conditions. Nevertheless, there is no reason why such information should not become available in due course and the potential of these catalysts in fuel processing and fuel cells could then be realised.

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