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A golden future for green chemistry

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Abstract

Interest continues unabated in catalysis by gold. It is now recognised that gold has unique properties as a catalyst for many reactions with pre-eminence established now in both heterogeneous and homogeneous processes. Indeed, gold catalysts can carry out processes for which no other catalyst has yet been identified. This paper sets out the general content of a keynote lecture delivered at the third world congress on gold in Limerick in 2006. In particular, aspects of the progress achieved since the second world congress, held in Vancouver in 2003, will be addressed. This is not an exhaustive statement on the progress achieved or the state of the field, since time did not permit such an exposition, and hence this is a personal perspective on gold catalysis and its potential impact on green chemistry.

Keywords: Gold catalysis; Green chemistry; Potential impact

1. Introduction

On Sunday 3 September 2006 over 300 delegates met in Limerick to discuss the emerging field of catalysis by gold. Since the previous meeting that had been held in Vancouver in September 2003 [1–4] there have been dramatic advance in catalysis by gold. It should be recognised that there is a great deal of excitement in the realisation that gold has previously unrecognised properties. The discovery in the 1980s that finely supported divided nanoparticles of gold could act as catalysts for reactions at low temperatures has to be one of the most fascinating observations of the late twentieth century, since hitherto gold had been considered unreactive and consequently most would consider that its chemistry was particularly unexciting. Indeed most text books dealing with inorganic chemistry gave scant regard to the chemistry of gold. Of course as a bulk metal it is chemically uninteresting, yet it has been the subject of dreams and the basis of fantastic treasure since its discovery as a beautiful ductile metal. Gold in a nanocrystalline state becomes incredibly reactive and this is the basis of many new discoveries. The intention of this paper is to briefly summarise the keynote lecture and to provide a personal perspective on the progress in the last 3 years.

As I was the first to speak I reflected on which of the locations for the Gold conferences (Gold 2001, Cape Town; Gold 2003, Vancouver; Gold 2006, Limerick) had been closet to gold mining. To the surprise of many the answer to this appears to be Limerick as a mining permit had been granted within 10 miles of the city. So perhaps Limerick has the best claim to hold such a meeting, although none should be surprised as Irish gold, especially historic gold artefacts, are very famous.

In this paper I will reflect on the advances in heterogeneous catalysis, but it must be noted that in the last 3 years there has, perhaps, been much more progress in the field of homogeneous catalysis [2,5], and the recent Hashmi reaction for phenol synthesis is a particularly good example of developments in this field that are inspiring new developments [6].

2. Gold catalysis and green chemistry

Green technology is a topic that is receiving significant attention as more and more people start to consider the importance of environmental issues. Many view catalysis as inherently green technology. However, one has to take a cradle to grave attitude to an chemical process. When this is done many catalysts may be made in a non-green manner, although when used they replace stoichiometric reagents and so overall they are at best partially green. In recent years catalysis by gold has stated to play a major role with respect to green chemistry

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and examples can be readily found that address the following 8 out of the 12 principles of green chemistry:

- prevent waste;
- design less hazardous chemical syntheses;
- use renewable feedstocks;
- use catalysts, not stoichiometric reagents;
- maximize atom economy;
- use safer solvents and reaction conditions;
- increase energy efficiency;
- minimize the potential for accidents.

In particular there are major examples of recent developments for hydrogenation and oxidation chemistry and this will be discussed.

3. Recent advances in hydrogenation

Although gold is now being extensively investigated for both selective and total oxidation reactions, there has been much less attention given to the activity and selectivity of selected gold catalysts for hydrogenation reactions. Even today there are few groups working on selective hydrogenation as compared with the extensive research activity presently devoted to the oxidation of CO. This is surprising since it has been shown in recent studies that supported gold catalysts can show very high selectivity for the hydrogenation of α,β-unsaturated aldehydes [7,8] and much of this work has recently been reviewed by Claus [9].

Very recently, Corma and Serna [10] have demonstrated the regioselective selective reduction of a nitro group when other reducible functions are present using gold nanoparticles supported on TiO_2 or Fe_2O_3. The chemoselective hydrogenation of functionalised nitroarenes with H_2 under mild reaction conditions was demonstrated providing a previously unknown route for the synthesis of the industrially important cyclohexanone oxime from 1-nitro-1-cyclohexene. In a related perspectives article, Blasser [11] noted that the "newly discovered gold catalysts are a welcome addition to the toolbox for chemoselective catalytic reduction of nitro compounds with hydrogen-sensitive substituents". Hence this exciting discovery of a new reaction for gold catalysts heralds a new phase for catalyst and reaction discovery. The key aspect of this discovery is that very little by-products are observed and these have represented a substantial problem and challenge for researchers who focused on the use of supported Pt catalysts [12]. Corma and Serna opted not to modify a known catalyst but tried gold for which there was no precedent for this reaction.

4. Selective oxidation using gold and gold-palladium catalysts

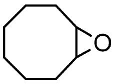
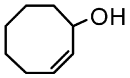
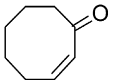
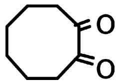
One of the key requirements for green chemistry is the need to utilise bio-renewable feedstocks. In this sense glycerol is a prime example since it is a major by-product from the manufacture of biodiesel. It was shown in 2002 that Au/C, with fairly large particle sizes (5–25 nm, multiply twinned crystals) could oxidise glycerol to glycerate using oxygen as the oxidant with 100% specificity, but only under aqueous basic conditions [13]. In a subsequent recent study the same catalyst has been shown to be effective for the epoxidation of cyclic alkenes with oxygen under mild, solvent free conditions [14]. In particular, no sacrificial hydrogen is required to achieve the selective oxidation (Table 1).

There have been significant developments in the direct synthesis of hydrogen peroxide using non-hazardous conditions and the oxidation of alcohols to aldehydes under solvent free conditions and hence both a welcome additions to the field of green chemistry. These will be described in the next sections.

4.1. Direct synthesis of hydrogen peroxide

Hydrogen peroxide is a key commodity chemical and at present most is used as a bleach or cleaning agent. Only a relatively small amount is used as an oxidant in fine chemicals synthesis, but from the perspective of chemists it is its potential use as a green oxidant that attracts attention. At present, hydrogen peroxide is produced by the sequential hydrogenation and oxidation of an alkyl anthraquinone. However, there are problems associated with the anthraquinone route which include the cost of the quinone solvent system and the requirement for periodic replacement of anthraquinone due to hydrogenation. In addition, the process is only economically viable on a relatively large scale (4–6 × 10^4 tpa), and this necessitates the transportation and storage of concentrated solutions of hydrogen peroxide when required for use in the fine chemicals industry since only relatively small amounts are required at any one time. Transport of such a hazardous material is not without risk and for this reason there is a genuine

Table 1
cis-Cyclooctene oxidation with molecular oxygen in the absence of a solvent [14]

Catalyst	TBHP (g)	Concentration (%)	Selectivity (%)				
							$\sum_{sel}C_8$
1% Au/graphite	0.12	7.9	81.2	9.3	4.1	0.5	95.1
1% Au/graphite	0.02	7.1	79.2	6.8	3.0	0.5	89.5
1% Au/graphite	0.002	1.3	82.6	7.4	2.1	0.6	92.7
No catalyst	0.008	2.0	Trace	0.0	0.0	0.0	–
Graphite	0.008	2.3	Trace	0.0	0.0	0.0	–

Reaction conditions: 0.12 g catalyst, *cis*-cyclooctene (10 ml, 0.066 mol), 80 °C, 24 h, in a stirred autoclave with O_2 3 bar. TBHP = *tertiary*-butylhydroperoxide.

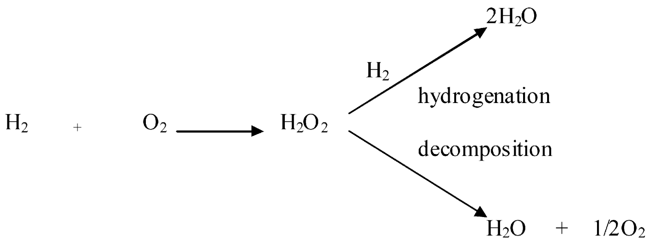
Table 2
The effect of catalyst calcination and/or reduction treatment on H_2O_2 synthesis [18]

Catalyst	Pretreatment	Productivity (mol-H_2O_2/h/Kg_{cat})	H_2O_2 (wt%)	H_2 conversion (%)	H_2O_2 selectivity (%)
2.5% Pd/TiO_2	Air, 25 °C	90	0.180	38	48
5% Pd/TiO_2	Air, 25 °C	173	0.346	86	40
2.5% Au-2.5% Pd/TiO_2	Air, 25 °C	202	0.404	46	89
5% Pd/TiO_2	Air, 200 °C, 3 h	99	0.198	42	47
2.5% Au-2.5% Pd/TiO_2	Air, 200 °C, 3 h	124	0.248	34	73
2.5% Pd/TiO_2	Air, 400 °C, 3 h	24	0.048	19	25
5% Pd/TiO_2	Air, 400 °C, 3 h	31	0.062	29	21
2.5% Au-2.5% Pd/TiO_2	Air, 400 °C, 3 h	64	0.128	21	61
2.5% Au-2.5% Pd/TiO_2	Air, 400 °C, 3 h + H_2, 500 °C	32	0.064	nd	nd

Reaction time 30 min; mass of catalyst 10 mg; nd, not determined.

quest to use a direct synthetic process that will be amenable to small scale synthesis at the point where it is required to be used. Hence the development of a new, highly efficient and smaller scale manufacturing process for H_2O_2 is of significant commercial interest.

In 2002 we showed that Au/Al_2O_3 catalysts were effective for the direct reaction [15]. However, the major discovery was the observation that the direct synthesis of H_2O_2 was significantly enhanced by using Au–Pd alloys supported on alumina and these catalysts significant improvements in the rate of hydrogen peroxide formation when compared with the Pd or Au only catalysts [15,16] The direct synthesis of hydrogen peroxide remains one of the most challenging targets concerning the control of reaction selectivity for a heterogeneously catalysed reaction.



In recent years, Ishihara et al. [17] have shown that Au/SiO_2 and Au-Pd/SiO_2 catalysts were also effective for this reaction. Recently, we have shown that the selectivity for H_2 utilisation can be significantly enhanced when Fe_2O_3 and TiO_2 are used as supports [18–20]. Indeed, at short reaction times the selectivity can be >95% for the reaction of dilute H_2/O_2 mixtures (1:1,

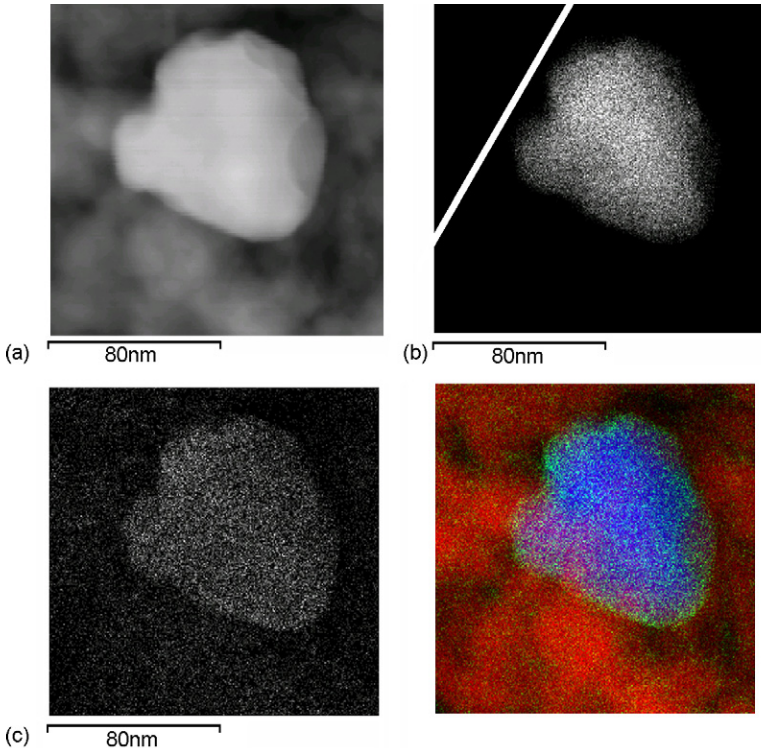


Fig. 1. STEM-ADF image of 2.5 wt% Au-2.5 wt% Pd/TiO_2 catalyst calcined at 400 °C, showing large alloy particle (a), Au M_2 STEM-XEDS map (b), Pd L_1 STEM-XEDS map (c); note that the Pd signal appears to originate from a larger area than that of the Au signal as demonstrated in the STEM colour map: blue = gold, green = palladium and red = titanium [28]. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of the article.)

5 vol%) diluted with CO_2 (95%). Very high rates of reaction were observed with non-calcined Au-Pd/TiO_2 catalysts (Table 2), but these catalysts were unstable losing both Au and Pd during reaction, and they could not be successfully reused. However, if the catalysts are calcined at 400 °C prior to use then very stable reusable catalysts are obtained. Detailed structural investigation of these active stable catalysts using XPS and transmission electron microscopy showed that the catalysts exhibited a core shell structure with a gold rich core and a palladium rich shell, and it was concluded that the Au was acting as an eletronic promoter for the Pd-rich surface of the Au–Pd nano-crystals (Fig. 1).

4.2. Oxidation of alcohols

The oxidation of alcohols and polyols to chemical intermediates represents a demanding target and is of immense importance for the production of fine chemicals. Glycerol is a highly functionalised molecule that is readily available from biosustainable sources, and as noted above supported gold catalysts readily achieve selective oxidations for this substrate. This field of gold catalysis has been based on the seminal studies of the Milan research groups of Rossi and Prati and co-workers [21–24] who have shown that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols, including diols, particularly when used under basic conditions.

One of the most significant advances in the field of alcohol oxidation has been the observations of Corma and co-workers [25,26] showing that an Au/CeO_2 catalyst is active for the selective oxidation of alcohols to aldehydes and ketones and the oxidation of aldehydes to acids. In these studies the catalysts are active at relatively mild conditions, without the addition of a solvent, using O_2 as oxidant without the requirement for the addition of NaOH to achieve high activity. This represents a key difference from the earlier studies concerning alcohol oxidation. The results were shown to be comparable to, or higher than, the highest activities that had been previously observed with supported Pd catalysts [27]. The catalytic activity was ascribed to the Au/CeO_2 catalyst stabilising a reactive peroxy intermediate from O_2. Indeed this was a major aspect of the catalyst design study since it is known that peroxy species can be selective for alcohol oxidation.

At much the same time the observation that supported gold–palladium alloys were effective catalysts for the production of hydrogen peroxide led us to conclude that these catalysts (Fig. 1; Table 2) could also be active for the oxidation of alcohols selectively to aldehydes. This was the case and we subsequently showed [28] that alloying Pd with the Au in supported Au/TiO_2 catalysts enhanced the activity for alcohols under solvent free conditions by a factor of over 25 as compared with the most active Au or Pd catalysts (Fig. 2). With these reactive catalysts primary alcohols and diols can be readily oxidised, further extending the scope of selective oxidation reactions that are possible with gold catalysts.

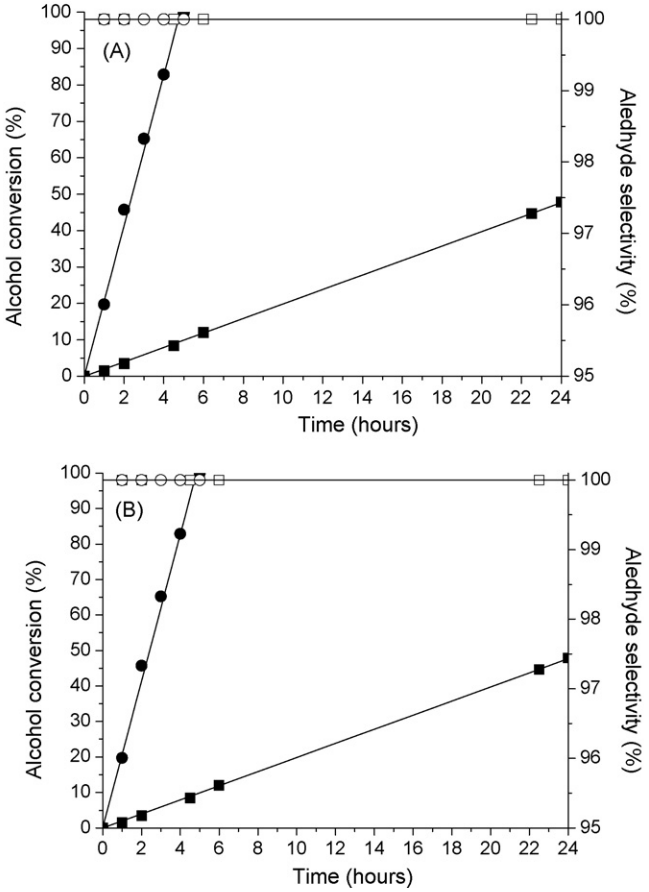


Fig. 2. (A) Benzyl alcohol conversion and selectivity in benzaldehyde with the reaction time at 373 K, 0.1 MPa O_2 pressure: (■) Au/TiO_2, (●) Pd/TiO_2, (▲) Au-Pd/TiO_2; solid symbols—conversion, open symbols—selectivity. (B) Catalyst Au-Pd/TiO_2 reactions at 363 K, 0.1 MPa O_2 pressure for: (■) cinnamyl alcohol and (●) vanillyl alcohol; solid symbols—conversion, open symbols—selectivity to the corresponding aldehydes [28].

5. Concluding comments

The field of catalysis by gold is now emerging as a hot field. Every few weeks, major new discoveries are being announced. Such is the pace of discovery that any review is likely to be out of date very rapidly. At present a large amount of effort is still focussed on the well documented oxidation of CO at ambient temperature, and a major debate remains concerning the nature of the active site and the mechanism of the reaction. However, it is clear that supported gold catalyst, whether prepared by coprecipition, deposition precipitation or impregnation, can be highly effective for other hydrogenation and oxidation reactions. The question is what new discoveries await us; we certainly do live in exciting times.

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