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Direct synthesis of hydrogen peroxide using ceria-supported gold and palladium catalysts

Edwin N. Ntainjua[a], Marco Piccinini[a], James C. Pritchard[a], Jennifer K. Edwards[a], Albert F. Carley[a], Christopher J. Kiely[b], Graham J. Hutchings[a,*]

[a] Cardiff Catalysis Institute, Cardiff University, School of Chemistry, Main Building, Park Place, Cardiff, CF10 3AT, UK
[b] Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA

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ABSTRACT

A key discovery in the last two decades has been the realisation that gold, when prepared as supported nanoparticles, is exceptionally effective as a redox catalyst. The catalytic efficacy is enhanced further by the alloying of gold with palladium and this is particularly exemplified for the direct synthesis of hydrogen peroxide where supported gold palladium alloy nanoparticles are found to be highly active. In this paper we report a study of ceria-supported gold, palladium and gold–palladium nanoparticles for the direct synthesis of hydrogen peroxide and show that ceria can be a potentially interesting support for this reaction. However, with current methods of catalyst fabrication ceria-supported monometallic palladium catalysts have a superior performance to bimetallic gold–palladium catalysts.

1. Background

This paper is dedicated to the memory of David Trimm who was an inspirational scientist who wrote a defining book on catalyst design that has served as a benchmark for many years [1]. My first meeting with David was at the first Natural Gas Conversion meeting in New Zealand in 1987. More specifically, I was introduced to David and Jens Rostrup-Nielsen at the hotel in Taranaki where he was enjoying one of Scotland's best loved exports. There followed a friendship that lasted the next twenty three years with him visiting us in the UK regularly. The last meeting was in Sapporo in July 2010 where he was in fine form and we shared a drink and anecdotes together. I discussed with him some recent work we were doing on hydrogen peroxide using supported gold–palladium nanoparticles and hence it is fitting that this becomes the subject of this paper in his memory. Indeed, the theme of this issue is "Catalysis for Energy and Clean Environment" and the direct synthesis of hydrogen peroxide fits both aspects. First, hydrogen peroxide can be used as a fuel both for rockets and more recently cars for high speed trials, and secondly the identification of a new direct synthesis route will enable local production of hydrogen peroxide at the point of use thereby aiding an improved environment.

2. Introduction

Over 3 million metric tonnes of hydrogen peroxide (H_2O_2) are produced annually. For example, in 2005 alone, 3.53 million metric tonnes H_2O_2 were produced globally and the demand in North America and Europe is growing by ca. 3–5% per year [2]. H_2O_2 is mainly used in bleaching and disinfecting applications and there is growing interest in its use as a green oxidant for chemical synthesis. Increasing legislative pressure to limit the use of chlorine for bleaching applications will ensure that the demand for H_2O_2 will continue to increase further. H_2O_2 is currently produced on a commercial scale via the indirect anthraquinone process which needs a very high capital investment as it requires to be carried out on a large scale for economic reasons [3]. In addition, there are other problems associated with the indirect process, including the low but significant losses of the expensive anthraquinone. The process has, however, been operated over several decades and has been highly optimised over this timeframe. The direct synthesis of H_2O_2 from molecular H_2 and O_2 represents a potentially greener alternative to the current anthraquinone process as it offers high atom efficiency, waste-free product, the possibility of using less or no organic solvents and lower energy consumption. The direct process also eliminates the risk of accidents associated with the transportation of concentrated H_2O_2 solutions [4] (>50% H_2O_2 produced by the anthraquinone process) as dilute solutions of H_2O_2 can be produced at the point of use using this simplistic and cheaper approach.

Although a large number of industrial [5–12] and academic [13–23] studies on the direct synthesis of H_2O_2 have been carried

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* Corresponding author.
E-mail addresses: hutch@cf.ac.uk, hutch@cardiff.ac.uk (G.J. Hutchings).

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out since it was first reported by Henkel and Weber in 1914, the process has still not been commercialised. The major challenge is to develop catalysts that will selectively produce H_2O_2 in preference to H_2O and, furthermore, are inactive for subsequent hydrogenation/decomposition of H_2O_2 as it is produced. Most catalysts reported so far fall short of these requirements as they also tend to be active for the undesired side reactions. To date, the most widely studied catalyst for the direct synthesis reaction comprise supported Pd nanoparticles. We have previously shown that the addition of Au to Pd significantly enhances the activity and selectivity of the catalyst as Au plays a role in limiting the undesired hydrogenation/decomposition of H_2O_2. By comparing the activity of monometallic Pd and Au catalysts with the activity of Au–Pd bimetallic catalysts we have shown that a synergistic effect exists between Au and Pd when both metals are present on supports such as carbon [18], TiO_2 [19,20], Al_2O_3 [21] or Fe_2O_3 [22]. The origin of this synergistic effect, in relation to catalyst structure, is still not fully understood, but are considered to originate from alloy formation leading to an electronic enhancement that increases the catalyst activity.

With respect to gold catalysis there has been much interest in the use of ceria as a catalyst support. Indeed it has been shown to be a very active support for gold nanoparticles for a range of reactions including alcohol oxidation and CO oxidation [24–30]. In view of this we have investigated ceria as a support for the direct synthesis of hydrogen peroxide and in this study we report our initial results using ceria-supported Au–Pd catalysts.

3. Experimental

3.1. Catalyst preparation

Catalysts comprising 2.5 wt% Au/2.5 wt% Pd/support were prepared using the following standard method (all quantities stated are per g of finished catalyst) $PdCl_2$ (0.042 g, Johnson Matthey) was added to an $HAuCl_4{\cdot}3H_2O$ solution (2.5 ml, 5 g in 250 ml) and stirred at 80 °C until the $PdCl_2$ dissolved. The support (0.95 g; CeO_2, Aldrich) was then added to the solution and stirred to form a paste. The support was either used in an un-treated form or it was acid pre-treated using 2% HNO_3 as described previously [18]. The paste was dried (110 °C, 16 h) before calcination (400 °C, 3 h). Monometallic 5 wt% Au and 5 wt% Pd-supported catalysts were prepared using both the untreated and acid pre-treated CeO_2 support in a similar way using appropriate amounts of $PdCl_2$ or $HAuCl_4{\cdot}3H_2O$ solution and support. Deionised water (2–3 ml) was used to dissolve the $PdCl_2$ for the preparation of Pd-only supported catalysts. In addition a range of 5% $PdCl_2$ on a range of supports were prepared as previously described for carbon [18], TiO_2 [19,20], Al_2O_3 [21] or Fe_2O_3 [22].

3.2. Catalyst testing

Hydrogen peroxide hydrogenation was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. To test each catalyst for H_2O_2 hydrogenation, the autoclave was charged with catalyst (0.01 g) and a solution containing 4 wt% H_2O_2 (5.6 g MeOH, 2.22 g H_2O and 0.68 g H_2O_2 (50%)). The charged autoclave was then purged three times with 5% H_2/CO_2 (0.7 MPa) before filling with 5% H_2/CO_2 to a pressure of 2.9 MPa at 20 °C. The temperature was allowed to decrease to 2 °C followed by stirring (at 1200 rpm) of the reaction mixture for 30 min. The wt% of H_2O_2 hydrogenated or decomposed was determined by titrating aliquots of the fresh solution and the solution after reaction with acidified $Ce(SO_4)_2$ (0.0288 M) in the presence of two drops of ferroin indicator.

Synthesis of H_2O_2 from H_2 and O_2 was performed under similar conditions in the presence of O_2 and with no added H_2O_2 (5% H_2/CO_2 and 25% O_2/CO_2, 1:2 H_2/O_2 at 3.7 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst and 1200 rpm). H_2O_2 productivity was determined by titration of the final filtered solution as described previously. H_2 conversion was calculated by gas analysis before and after reaction using a GC with TCD and CP, Carboplot P7 column (25 m, 0.53 mm i.d.).

4. Results and discussion

4.1. Ceria-supported monometallic Pd catalysts for direct H_2O_2 synthesis

For the initial part of our study we compared the activity of mono-metallic supported Pd catalysts for the direct synthesis of hydrogen peroxide using standard reaction conditions and the results are shown in Table 1. It is apparent that supporting Pd on ceria leads to the most active Pd catalyst of the series of supports tested. Supported Pd catalysts tend to be much more active than supported Au catalysts and 5% Pd/CeO_2 is about an order of magnitude more active than any supported Au catalyst [18–22]. This demonstrates that ceria could potentially be a very interesting support for this reaction. It is possible that the defective nature of the ceria support aids the dispersion of the Pd nanoparticles. This postulate is currently under investigation by electron microscopy, although imaging nanoscale Pd clusters on a high mass support such as CeO_2 is a non-trivial exercise. We are currently attempting this type of study using the latest aberration corrected scanning transmission electron microscopy techniques.

4.2. Effect of Au addition to CeO_2-supported Pd catalyst for the direct formation and hydrogenation of H_2O_2

We have previously shown that the addition of Au to Pd catalysts supported on carbon [18], TiO_2 [19,20], Al_2O_3 [21] or Fe_2O_3 [22] leads to a significant increase in the H_2O_2 synthesis activity as Au acts to limit the subsequent hydrogenation/decomposition of H_2O_2. Hence a marked synergistic effect between Au and Pd for H_2O_2 formation is observed over these catalysts (Fig. 1). The direct formation and hydrogenation of H_2O_2 over CeO_2-supported Au-only, Pd-only and Au–Pd catalysts is shown in Table 2. The addition of Au to Pd resulted in a decrease in H_2O_2 hydrogenation activity in agreement with our previously reported [18–23] Au and Pd catalysts. In contrast with our previous findings and surprisingly, Au addition also led to a considerable decrease in both H_2O_2 synthesis activity and H_2O_2 selectivity irrespective of the decrease in H_2O_2 hydrogenation/decomposition activity. Fig. 1 shows that while there is a synergistic effect between Au and Pd for H_2O_2 synthesis over Al_2O_3,

Table 1
H_2O_2 synthesis and hydrogenation using supported Pd catalysts.

Catalyst	H_2O_2 productivity[a] ($mol_{H_2O_2}$ kg_{cat}^{-1} h^{-1})	H_2O_2 hydrog.[b] ($mol_{H_2O_2}$ kg_{cat}^{-1} h^{-1})
5% Pd/Al_2O_3	12	200
5% Pd/Fe_2O_3	4	nd
5% Pd/TiO_2	31	288
5% Pd/C	55	135
5% Pd/CeO_2	97	329

[a] Rate of hydrogen peroxide production determined after reaction using standard reaction conditions: 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 8.5 g solvent (5.6 g MeOH + 2.9 g H_2O), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

[b] Rate of hydrogenation of H_2O_2 calculated from amount of H_2O_2 hydrogenated using standard reaction conditions: 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 8.5 g solvent (5.6 g MeOH + 2.22 g H_2O and 0.68 g 50% H_2O_2), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

Table 2
H_2O_2 synthesis, hydrogenation and selectivity over CeO_2-based supported Pd, Au and Au–Pd catalysts.

Catalyst	H_2O_2 productivity[a] ($mol_{H_2O_2}\ kg_{cat}^{-1}\ h^{-1}$)	H_2O_2 hydrog.[b] ($mol_{H_2O_2}\ kg_{cat}^{-1}\ h^{-1}$)	H_2 conversion[c] (%)	H_2O_2 selectivity[d] (%)
CeO_2	0	88	nd	nd
5% Au/CeO_2	1	118	nd	nd
5% Pd/CeO_2	97	329	31	43
2.5% Au 2.5% Pd/CeO_2	68	212	31	30

[a] Rate of hydrogen peroxide production determined after reaction using standard reaction conditions: 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 8.5 g solvent (5.6 g MeOH + 2.9 g H_2O), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

[b] Rate of hydrogenation of H_2O_2 calculated from amount of H_2O_2 hydrogenated using standard reaction conditions: 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 8.5 g solvent (5.6 g MeOH + 2.22 g H_2O and 0.68 g 50% H_2O_2), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

[c] H_2 conversion measured by difference between H_2 concentration before and after reaction.

[d] H_2O_2 selectivity calculated using: H_2O_2 selectivity = (moles H_2O_2 formed/moles H_2O_2 converted) × 100.

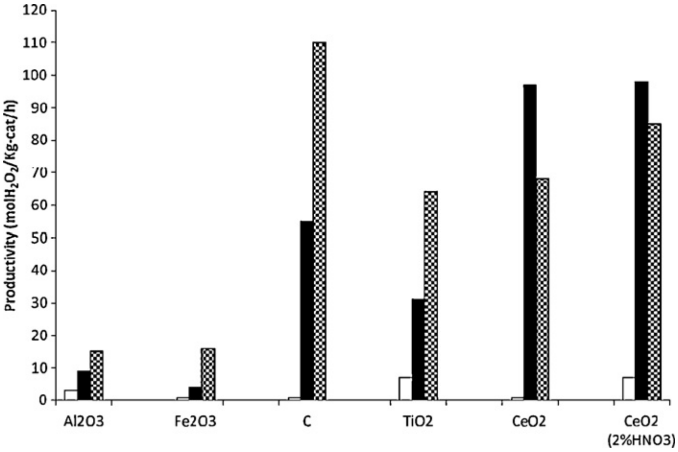

Fig. 1. Plot showing synergy versus no synergy for supported Au and Pd catalysts for the direct synthesis of hydrogen peroxide. 5% Au (☐), 5% Pd (■), 2.5% Au–2.5% Pd (▩).

Fe_2O_3, carbon and TiO_2-based catalysts, the CeO_2-based catalysts show no synergy between Au and Pd.

4.3. *Effect of calcination temperature on the activity of ceria-supported catalysts*

Table 3 shows the effect of calcination temperature on the H_2O_2 synthesis and hydrogenation activity of the Pd/CeO_2 and Au–Pd/CeO_2 catalysts. While the monometallic Pd catalyst surprisingly showed an increase in H_2O_2 synthesis activity (in agreement with decreasing H_2O_2 hydrogenation activity) with increasing calcination temperature, the Au–Pd catalyst showed a slight decrease in H_2O_2 synthesis activity with increasing calcination temperature regardless of the decrease in H_2O_2 hydrogenation activity. If we compare the H_2O_2 synthesis activity of the uncalcined Pd monometallic and uncalcined Au–Pd bimetallic catalysts on ceria, it is clear that a synergistic effect between Au and Pd does exist. However, this effect is lost upon calcination of the catalyst as this process seems to enhance the H_2O_2 synthesis activity of the Pd-only catalyst while slightly decreasing the H_2O_2 synthesis activity of the Au–Pd bimetallic catalyst.

Table 3
Effect of calcination temperature on the direct synthesis of H_2O_2 using Pd/CeO_2 and Au–Pd/CeO_2 catalysts.

Calcination temperature[a] (°C)	H_2O_2 productivity[b] ($mol_{H_2O_2}\ kg_{cat}^{-1}\ h^{-1}$)	H_2O_2 hydrogenation[c] ($mol_{H_2O_2}\ kg_{cat}^{-1}\ h^{-1}$)
5% Pd/CeO_2		
Uncalcined	58	639
200	46	624
400	97	329
2.5% Au–2.5% Pd/CeO_2		
Uncalcined	72	433
200	76	333
400	68	212

[a] Catalysts calcined in static air at different temperatures (0–400 °C) for 3 h.

[b] Rate of hydrogen peroxide production determined after reaction at 2 °C (all conditions same as defined in Table 1).

[c] Rate of hydrogenation of H_2O_2 calculated from amount of H_2O_2 hydrogenated at 2 °C (all other conditions same as defined in Table 1).

4.4. *Effect of acid pre-treatment of the CeO_2 support on the synthesis and hydrogenation of H_2O_2*

We have previously shown that acid pre-treatment of carbon [18] or TiO_2 [20] supports prior to impregnation with the Au and Pd salts leads to considerable improvement in the H_2O_2 synthesis activity and selectivity of the Au–Pd catalyst. Table 4 shows the effect of acid pre-treatment of the CeO_2 support on the activity and selectivity of CeO_2-based Au and Pd monometallic and Au–Pd bimetallic catalysts. While acid pre-treatment of the CeO_2 support did not affect the H_2O_2 synthesis activity and H_2O_2 selectivity for the Pd monometallic catalyst, the Au monometallic and Au–Pd bimetallic catalysts both showed an increase in H_2O_2 synthesis activity as a result of acid pre-treatment of the support. This increase in H_2O_2 synthesis activity can be attributed to the decrease in H_2O_2 hydrogenation/decomposition activity observed for the CeO_2-supported acid-pre-treated catalysts. We have previously shown [18] that Au–Pd catalysts synthesised using acid-pre-treated carbon leads to the formation of smaller nanoparticles which possibly decorate sites to inhibit/switch off H_2O_2 hydrogenation/decomposition. For the TiO_2-based acid pre-treated supported Au–Pd catalyst, we have also proposed an enhancement in Au dispersion as a possible reason for the observed promotional effect. It is apparent that the acid-pre-treatment of the ceria does enhance the activity of the Au-containing catalysts, which is in line with these previous observations. However, it does not enhance the activity of the AuPd bimetallic catalysts above the level of the Pd-only catalyst for the materials calcined at 400 °C, although interestingly, a positive effect is observed for the materials calcined at 200 °C. This is the first time that we have observed this curious effect.

4.5. *Re-usability of ceria-supported catalysts*

Fig. 2 shows catalyst reuse data for the Pd/CeO_2, Au–Pd/CeO_2 and the Au–Pd/CeO_2 acid pre-treated (2% HNO_3) catalysts that had been calcined at 400 °C for 3 h and all were observed to be re-usable. The uncalcined catalysts all showed a considerable decrease in H_2O_2 synthesis activity when re-used. As we have noted previously [19] the calcination step in the preparation method is therefore critical to improve catalyst stability and ensure that these catalysts are re-usable.

Table 4
Effect of acid pre-treatment of support on the direct synthesis of H_2O_2 over CeO_2-based supported Pd, Au and Au–Pd catalysts.

Catalyst	H_2O_2 productivity[a] ($mol_{H_2O_2}$ kg_{cat}^{-1} h^{-1})	H_2O_2 hydrog.[b] ($mol_{H_2O_2}$ kg_{cat}^{-1} h^{-1})	H_2 conversion[c] (%)	H_2O_2 selectivity[d] (%)
CeO_2 (2% HNO_3)	0	37	nd	nd
5% Au/CeO_2 (2% HNO_3)	7	63	nd	nd
5% Pd/CeO_2 (2% HNO_3)	98	329	30	45
2.5% Au 2.5% Pd/CeO_2 (2% HNO_3)	85	198	31	38

a, b, c and d same as defined in Table 2.

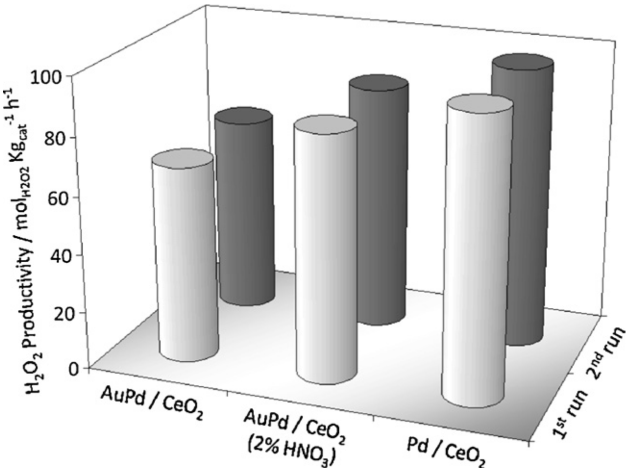

Fig. 2. Effect of catalyst re-use on the H_2O_2 synthesis performance of Pd/CeO_2 and Au–Pd/CeO_2 (untreated and acid pre-treated) catalysts.

5. Conclusions and comments on the lack of synergy for this system

It is clear from these initial studies that ceria could present a very interesting support for gold and palladium supported nanoparticles for the direct synthesis of hydrogen peroxide. The reason being that with the ceria-supported monometallic Pd catalyst very high activities are observed which are considerably higher than those found with other carbon- and oxide-supported monometallic Pd catalysts. However, the addition of Au to the ceria-supported catalysts does not enhance the activity markedly, although it does influence the rate of H_2O_2 hydrogenation. The origin of this effect is most likely to be due to lack of alloy formation under the reaction conditions we are using. Unfortunately, ceria is a difficult support on which to directly observe ultra-small Au and Pd particles using phase contrast and high angle annular dark field imaging techniques. In view of this, we are endeavouring to determine whether or not alloying is occurring using XEDS spectrum imaging in an aberration corrected scanning transmission electron microscope, and this will be the subject of a subsequent and more detailed investigation.

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