

The Direct Synthesis of Hydrogen Peroxide Using Platinum-Promoted Gold–Palladium Catalysts**

Jennifer K. Edwards,* James Pritchard, Li Lu, Marco Piccinini, Greg Shaw, Albert F. Carley, David J. Morgan, Christopher J. Kiely, and Graham J. Hutchings*

Abstract: The direct synthesis of hydrogen peroxide offers a potentially green route to the production of this important commodity chemical. Early studies showed that Pd is a suitable catalyst, but recent work indicated that the addition of Au enhances the activity and selectivity significantly. The addition of a third metal using impregnation as a facile preparation method was thus investigated. The addition of a small amount of Pt to a CeO₂-supported AuPd (weight ratio of 1:1) catalyst significantly enhanced the activity in the direct synthesis of H₂O₂ and decreased the non-desired over-hydrogenation and decomposition reactions. The addition of Pt to the AuPd nanoparticles influenced the surface composition, thus leading to the marked effects that were observed on the catalytic formation of hydrogen peroxide. In addition, an experimental approach that can help to identify the optimal nominal ternary alloy compositions for this reaction is demonstrated.

The direct synthesis of hydrogen peroxide from hydrogen and oxygen offers a cleaner, more atom-efficient alternative to the current commercial production process for this important commodity chemical. Currently, over three million metric tons of H₂O₂ are produced from the indirect anthraquinone process, around 80 % of this amount is used for fine chemical synthesis and in the paper and textile bleaching industries.^[1] The increasing demand for propylene oxide means that the forecasted demand for H₂O₂ is predicted to exceed 4.3 million metric tons in 2015.^[2] The indirect process produces concentrated H₂O₂ that has to be transported to its point of use where it is diluted. The direct route would enable H₂O₂ production to take place at its point of use, and for this reason there is significant interest in developing such a catalytic process.^[3] An obvious challenge in the direct synthesis process is achieving high H₂ selectivity toward H₂O₂ and avoiding water formation by the sequential hydrogenation of H₂O₂. A number of catalysts have been investigated

for the direct synthesis of H₂O₂. The vast majority of them are based on supported Pd nanoparticles,^[3b,4] but these materials require the addition of acid and halide promoters in the reaction medium to achieve high selectivity at high conversions.^[3b,4d,5] We have shown that the incorporation of Au in Pd catalysts to form supported nanoalloys results in catalysts that synthesize H₂O₂ with high selectivities in the absence of acid and halide stabilizers.^[6] Clearly, the composition of the alloy catalyst is a major factor in catalyst design.^[6a,7] Recently, we have shown that the addition of Pt to the AuPd nanoalloy catalyst to form a trimetallic alloy has beneficial effects in the oxidation of benzyl alcohol.^[8] The use of Pt as a catalyst component in the direct synthesis process has also been considered previously by Strukul and co-workers.^[9] They synthesized Pd/Pt and Pd/Au nanoparticles supported on sulphated zirconia and compared the activity for the direct synthesis of H₂O₂ in the presence of acid. The addition of Pt to Pd enhanced the yield of H₂O₂, but the extent of the effect was highly sensitive to the concentration of Pt: by using a low Pt content it was possible to improve the H₂ selectivity from 55 to 70 %. However, the positive effect on H₂O₂ selectivity was not observed by Lunsford et al.,^[4c] who showed that the addition of 5 atom % Pt to a SiO₂-supported Pd (0.5 wt %) catalyst increased the H₂O₂ productivity by a factor of 2.5, but the selectivity was slightly lower than that of the monometallic Pd catalyst. This effect may be due to the presence of halide in the Lunsford study, and indeed, when halide was absent, the Pt/Pd catalysts produced only water. Clearly, the addition of Pt can have beneficial effects as a catalyst component in the direct-synthesis process. Herein we show that the addition of Pt to CeO₂-supported AuPd nanoalloy catalysts to form trimetallic catalysts can have marked effects on both the synthesis and hydrogenation of H₂O₂, and we demonstrate an experimental approach to identify the optimal nominal trimetallic catalyst composition for the synthesis of H₂O₂.

We prepared catalysts with 5 wt % total metal content using an impregnation method^[6d] and selected CeO₂ as a support, as we had previously shown this to be a suitable support material for AuPd nanoalloys.^[10] A series of CeO₂-supported mono- and bimetallic Au, Pd, and Pt catalysts were prepared—we have shown in our earlier study that the AuPdPt trimetallic compositions on TiO₂ or activated carbon supports form alloys containing all three component metals.^[8] The monometallic and bimetallic combinations of these catalysts were evaluated for the direct synthesis of H₂O₂, and the results for the initial rates after 2 min reaction and also for a standard reaction time of 30 min are shown in Table 1. The activities ranked in the order PdPt > Pd >

[*] Dr. J. K. Edwards, J. Pritchard, M. Piccinini, G. Shaw, Dr. A. F. Carley, D. J. Morgan, Prof. G. J. Hutchings
Cardiff Catalysis Institute, School of Chemistry
Cardiff University, Main Building
Park Place, Cardiff, CF10 3AT (UK)
E-mail: edwardsjk@cf.ac.uk
hutch@cf.ac.uk

L. Lu, Prof. C. J. Kiely
Department of Materials Science and Engineering
Lehigh University
5 East Packer Ave, Bethlehem, PA 18015 (USA)

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Table 1: Direct synthesis of H_2O_2 using CeO_2 -supported Au, Pd and Pt monometallic and Au-Pt, Au-Pd, Pd-Pt bimetallic catalysts, using standard reaction conditions.

	Composition [wt%]			Productivity [$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}$]		Hydrogenation [$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}$]
	Au	Pt	Pd	2 min	30 min	
1	5			n.d.	1	118
2		5		46	8	126
3			5	354	97	329
4	2.5	2.5		120	20	109
5	2.5		2.5	281	68	145
6		2.5	2.5	392	138	182

n.d. = not determined.

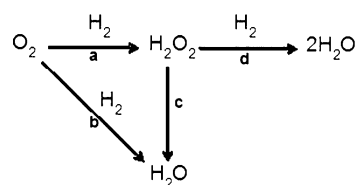
$\text{AuPd} > \text{AuPt} > \text{Pt} \gg \text{Au}$, showing, as expected, that Pd is the most active component for the direct synthesis. We also investigated the activity for the hydrogenation/decomposition of H_2O_2 after reaction for 30 min (Table 1), and it is apparent that all the monometallic and bimetallic catalysts are active for this reaction. However, it is also apparent that the addition of Pt to Au has a significant synergistic effect on both reactions using this support, which is more marked than that observed for the addition of Pd to Au. This result prompted us to study trimetallic combinations where we added small amounts of Pt to the catalyst while maintaining a constant Au:Pt ratio (Table 2). The addition of small amounts of the third metal significantly affects the activity, with some

Table 2: Direct synthesis of H_2O_2 using CeO_2 -supported Au, Pd, and Pt alloy catalysts under standard reaction conditions. This data shows the effect on productivity and hydrogenation of adding various amounts of Pt to Au/Pd catalysts, while keeping both the total metal loading and the Au:Pt ratio constant.

	Composition [wt%]			Productivity [$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}$]		Hydrogenation [$\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}$]
	Au	Pd	Pt	2 min	30 min	
1	2.50	2.50		281	68	145
2	2.48	2.48	0.05	308	63	46
3	2.45	2.45	0.10	171	109	76
4	2.40	2.40	0.20	436	170	145
5	2.35	2.35	0.30	389	159	177
6	2.28	2.28	0.45	670	100	459
7	2.00	2.00	1.00	194	115	93
8	2.50	2.30	0.20	260	86	11

compositions showing an enhancement, while others show a suppression in activity. Replacing some of the Pd by Pt showed that the activity could be enhanced while decreasing the hydrogenation/decomposition rate (compare entry 8 with entry 1 in Table 2). As the reactions were carried out in a batch reactor with stirring, the measured overall synthesis rate is a combination of both the total H_2O_2 synthesis rate and the sequential hydrogenation/decomposition rate for a fraction of the H_2O_2 produced (see Scheme 1).

We wanted to determine the optimal trimetallic composition for this reaction, with a maximized rate of synthesis and



Scheme 1. Reaction pathways involved in the direct reaction: a) synthesis, b) combustion, c) decomposition, and d) hydrogenation.

at the same time a minimized rate of sequential hydrogenation/decomposition reactions. To achieve this goal, we carried out an extensive range of experiments for the synthesis and hydrogenation/decomposition of H_2O_2 using CeO_2 -supported trimetallic catalysts that spanned a wide range of compositions (see the Supporting Information for the full tabulated data set, all compositions were prepared and tested in duplicate and the experimental error associated with each data point is $\pm 2\%$ of the stated value). The results were plotted graphically in Figure 1 where the activity value has been superimposed on a ternary composition diagram, with red signifying the most active nominal compositions. The

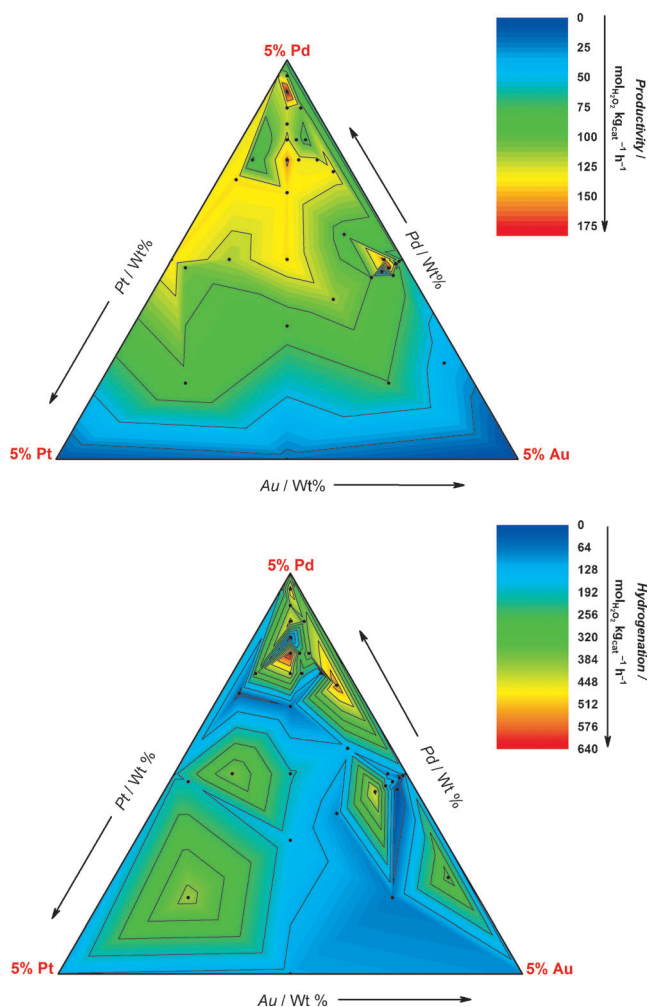


Figure 1. Rates of H_2O_2 synthesis and hydrogenation/decomposition for CeO_2 -supported 5 wt% Au/Pd/Pt catalysts presented as a contour diagram. a) Productivity b) hydrogenation/decomposition.

plot, summarizing the rate of synthesis versus nominal ternary composition (Figure 1a), shows that there are three potential nominal composition regions of interest (red), namely: 1) a composition that is essentially Pd with very small additional amounts of both Au and Pt; 2) a composition that also comprises mainly Pd (as in (1)) but contains more Au and Pt, and 3) a 1:1 composition of AuPd with a small additional amount of Pt. All of these three composition regions represent catalysts that are far more active than the bimetallic AuPd/CeO₂ catalysts. These results clearly demonstrate the promotional effect of adding a small amount of Pt to a AuPd alloy catalyst for the direct synthesis of H₂O₂. The rates for hydrogenation/decomposition are shown in Figure 1b, with compositional regions of low and high activity being represented by a blue and red coloration, respectively. It is apparent that the composition ranges (1) and (2), identified in Figure 1a, are also highly effective for the hydrogenation/decomposition reaction. Only composition range (3) shows real promise as an improved catalyst formulation as this has a high synthesis activity combined with low hydrogenation/decomposition activity.

In view of this result, we analyzed selected catalysts by X-ray photoelectron spectroscopy to determine if any specific surface features were responsible for the observed tendencies in activity. In Table 3, we report quantified surface molar Pd/

Table 3: XPS-derived molar surface Pd:Au ratios for selected CeO₂-supported catalysts. All catalysts were calcined in static air at 400 °C for 3 h, except: [a] dried at 110 °C and [b] calcined at 200 °C.

	Composition [wt %]			Reactivity		Pd/Au (molar ratio)	
	Au	Pd	Pt	Prod.	Hydrog.	Theo.	Exp.
1	2.50	2.50		68	145	1.9	7.1
2	2.40	2.40	0.20	170	145	1.9	58
3	2.275	2.275	0.45	100	459	1.9	37
4	0.625	3.75	0.625	153	439	11	48
5	2.30	2.50	0.20	155	94	2.0	135
6	2.50	2.30	0.20	86	11	1.7	165
7	2.275	2.275	0.45 ^[a]			1.9	0.9
8	2.275	2.275	0.45 ^[b]			1.9	5.8
9	2.275	2.275	0.45	100	459	1.9	37

All catalysts were calcined in static air at 400 °C for 3 h, unless stated otherwise. [a] Dried at 110 °C. [b] Calcined at 200 °C.

Au ratios derived from the XPS analyses of selected trimetallic catalysts, together with results for a CeO₂-supported 2.5 wt % Au/2.5 wt % Pd material for comparison. After calcination, the Pd/Au ratio is higher (7.1) than the value expected (1.9) for a homogeneous metal dispersion for the 1:1 bimetallic catalyst. This has been noted before on other metal oxide supported Au/Pd samples and has been shown by STEM-EDX studies to correlate with the formation of Au(core)/Pd(shell) nanoparticles^[7a] What is striking is the dramatic further increase in the Pd/Au ratio resulting from the addition of a small amount of Pt; for example, the ratio for the 2.4 wt % Au/2.4 wt % Pd/0.20 wt % Pt catalyst increases to a value of 58. Similar unexpectedly high Pd/Au ratios are observed for all the Pt-promoted samples (Table 3). This

effect could be caused either by the core-shell effect being enhanced by the presence of Pt, or by a significant Pt-induced redispersion of Pd on the surface. Also shown in Table 3 are data for the 2.275 wt % Au/2.275 wt % Pd/0.45 wt % Pt catalyst after heat treatment, reflecting the evolution of the core-shell structure (increasing Pd/Au value) with increasing calcination temperature. Productivity and hydrogenation data are also included where available in Table 3 for reference, and it is apparent that both the surface composition and hence reactivity can be manipulated by the addition of a third metal in these supported metal catalysts. To determine whether the enhancement in catalytic performance is due to the core-shell effect detected by XPS or whether the metal dispersion was the key factor, we have carried out an additional experiment. We have determined the particle size distributions for two samples, namely 2.5 wt % Au/2.5 wt % Pt/CeO₂ and 2.4 wt % Au/2.4 wt % Pd/0.2 wt % Pt/CeO₂ (see Figures S1 and S2 in the Supporting Information), which show a distinct contrast in catalyst performance (Table 1). Both catalysts comprise small particles in the range 1–5 nm and the particle size distributions are broadly similar with the 2.5 wt % Au/2.5 wt % Pt/CeO₂ catalyst having a mean particle size of 1.2 nm and 2.4 wt % Au/2.4 wt % Pd/0.2 wt % Pt/CeO₂ catalyst having a mean particle size of 1.5 nm. The observation that the particle size increases slightly on addition of Pt shows that the enhancement in activity is not associated with the metal dispersion, and hence the electronic effect induced on addition of the third metal through the formation of core-shell structures is considered to be the origin of the effect we observed.

In summary, we have shown that the addition of a small amount of Pt to a AuPd catalyst (weight ratio of 1:1) significantly enhances its activity in the direct synthesis of H₂O₂. The addition of Pt to the AuPd nanoparticles significantly affects the surface composition, leading to the marked effects observed on the catalytic formation of hydrogen peroxide. In addition, we have demonstrated an experimental approach that can help to identify the optimal nominal ternary alloy compositions for this reaction by studying the synthesis and hydrogenation/decomposition reactions as separate data sets and superimposing the activity values as a fourth (vertical) dimension on a ternary composition diagram.

Experimental Section

Caution! These experiments involve high pressures.

Au, Pd, and Pt catalysts were prepared using an incipient wetness method. Supported AuPdPt, AuPd, PdPt, AuPt, Au, Pd, and Pt catalysts (5 wt % total metal content) were synthesized by standard wet impregnation methodology. For a 2.5 wt % Au/2.5 wt % Pd catalyst, the following standard procedure was adopted, with all quantities listed per gram of catalyst. PdCl₂ (0.042 g) was dissolved in a solution of H₂AuCl₄·3H₂O (2.05 mL, 12.25 g Au in 1000 mL; [Au] = 62 mM) while stirring at 80 °C until the Pd dissolved completely. CeO₂ (nanograde, Aldrich) was then added to the solution and stirred at 80 °C to form a thick paste. The material was dried (110 °C, 16 h) and subsequently calcined in static air (400 °C, 3 h). Monometallic Au and Pd were synthesized using the same protocol. For the synthesis of supported 5 wt % Au/Pd/Pt catalysts, a solution of H₂PtCl₆ (1.0 g Pt in

25 mL) was introduced by wet impregnation in conjunction with the Au and Pd metal precursor salts, with the amount added depending on the intended nominal mono-, bi-, or trimetallic catalyst composition.

The catalysts were evaluated for the direct synthesis of H_2O_2 in a stainless steel autoclave (Parr Instruments) with a nominal volume of 100 mL and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and provision for measurement of temperature and pressure. For the standard reaction conditions, the autoclave was charged with the catalyst (0.01 g) and solvent (5.6 g CH_3OH and 2.9 g H_2O), purged three times with 5 % H_2/CO_2 (0.7 MPa), and then filled with 5 % H_2/CO_2 and 25 % O_2/CO_2 to give a hydrogen to oxygen ratio of 1:2 at a total pressure of 4.0 MPa. Stirring (1200 rpm) was commenced on reaching the desired temperature (2 °C), and experiments were carried out for 30 min. The H_2O_2 yield was determined by titration of aliquots of the final filtered solution with acidified $\text{Ce}(\text{SO}_4)_2$ ($7 \times 10^{-3} \text{ mol L}^{-1}$). The $\text{Ce}(\text{SO}_4)_2$ solutions were standardized against $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ using ferroin as an indicator. Hydrogenation experiments were carried out as outlined above, but in the absence of 25 % O_2/CO_2 in the gas stream and with the presence of 4 wt % H_2O_2 in the solvent (solution composition: 5.6 g CH_3OH , 2.22 g H_2O , 0.68 g 50 wt % H_2O_2). The decrease in H_2O_2 concentration (as determined from measurements taken before and after the reaction) is attributed to a combination of H_2O_2 hydrogenation and decomposition.

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