# Catalysis Science & Technology

# PAPER

Cite this: Catal. Sci. Technol., 2013, 3, 2910

# Physical mixing of metal acetates: optimisation of catalyst parameters to produce highly active bimetallic catalysts

We have investigated the optimisation of the catalytic parameters for the preparation of catalysts by the simple

mixing and thermal treatment of a support and metal acetate precursors. We have studied the effect of metal

ratio and metal loading to produce a catalyst which has the optimum activity for a variety of reactions including benzyl alcohol oxidation, glycerol oxidation and the direct synthesis of hydrogen peroxide. We have demonstrated

the high activity of these catalyst's for a variety of substrates and performed XPS and XRD studies on the catalysts

Peter J. Miedziak,<sup>a</sup> Simon A. Kondrat,<sup>a</sup> Noreen Sajjad,<sup>ab</sup> Gavin M. King,<sup>a</sup> Mark Douthwaite,<sup>a</sup> Greg Shaw,<sup>a</sup> Gemma L. Brett,<sup>a</sup> Jennifer K. Edwards,<sup>a</sup> David J. Morgan,<sup>a</sup> Ghulam Hussain<sup>b</sup> and Graham J. Hutchings<sup>\*a</sup>

to help elucidate the origin of the catalysts improved activity.

Received 17th April 2013, Accepted 7th May 2013

DOI: 10.1039/c3cy00263b

www.rsc.org/catalysis

### Introduction

Heterogeneous catalysis is a key process in the manufacture of a range of bulk and fine chemicals and is at the heart of green chemical processes. The use of catalysts for oxidation reactions can lead to a greener process when compared with alternative routes. Gold nanoparticles have been shown to be effective for the oxidation of alkenes<sup>1–3</sup> alcohols,<sup>4,5</sup> the oxidation of CO<sup>6,7</sup> and for the direct synthesis of hydrogen peroxide.<sup>8</sup> It has also been demonstrated that alloying gold with palladium leads to a substantial enhancement in activity for alcohol oxidation<sup>9,10</sup> and also significantly improves the yield of hydrogen peroxide in the direct synthesis reaction.<sup>10,11</sup>

The catalysts reported for these oxidations are usually prepared by three main methods; namely, wet impregnation, deposition precipitation and sol-immobilisation. However, all these preparation techniques use HAuCl<sub>4</sub> as the gold precursor, making it difficult to completely remove chloride from the final catalyst. It is known that the presence of chloride in a catalyst can lead to particle agglomeration, through Au–Cl–Au bridges<sup>12</sup> and also leads to the blocking of active sites.<sup>13</sup> The result of these effects is a loss of catalyst activity, which is well documented for CO oxidation with gold monometallic catalysts.<sup>14,15</sup> It has been observed that a Cl/Au atom ratio of 0.1 is sufficient to decrease the activity by half for a CO oxidation catalyst, despite most of the Cl<sup>-</sup> being

Fax: +44 (0)29 2087 4059

associated solely with the Al<sub>2</sub>O<sub>3</sub> support. The blocking of sites on the Al<sub>2</sub>O<sub>3</sub> support with phosphate showed that a Cl:Au atom ratio even as low as 0.0006 could affect activity. A method of limiting chloride levels in catalysts involves tuning the pH of the deposition, to ensure significant hydrolysis of the HAuCl<sub>4</sub> and also to minimize Cl<sup>-</sup> deposition onto the support.<sup>15</sup> Unfortunately, a pH that facilitates total hydrolysis (~pH 10) also results in a decrease in the Au loading levels.<sup>15,16</sup> An alternative method of reducing chloride levels is by heat treatment of the catalyst, but unfortunately this causes agglomeration through sintering.15 Modification of the impregnation and deposition techniques by the addition of ammonia has also been shown to minimize Cl<sup>-</sup> content in catalysts to less than 200 ppm.<sup>17-19</sup> However, the addition of ammonia is undesirable in an applied scaled up process, due to its corrosive and toxic nature.

The simple physical mixing of metal acetates and subsequent heat treatment under an inert atmosphere has been shown to be effective for the formation of supported metal nanoparticles.<sup>20</sup> Recently we clearly demonstrated the potential for the chloride-free formation of supported Au and Au–Pd alloy catalysts by the physical mixing of metal acetates with a support.<sup>21</sup> The removal of aqueous chloride ions from the preparation medium significantly decreases the waste material and ensures that the catalyst preparation is completed in a greener manner. These Au–Pd alloy catalysts were shown to have exceptionally high activity, compared to wet impregnation and deposition precipitation techniques, for both the direct synthesis of hydrogen peroxide and benzyl alcohol oxidation. Although the preparation technique produced significant amounts of highly dispersed sub 10 nm

# **RSC**Publishing

**View Article Online** 

<sup>&</sup>lt;sup>a</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT UK. E-mail: hutch@cardiff.ac.uk;

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, University of Sargodha, Sargodha, 40100 Pakistan

particles, thought to be responsible for the high activity, large  $\mu$ m particles of Au and Pd were also observed.

In our previous work, we showed that catalysts that were analogous in terms of metal ratio and weight loading to previously reported optimised catalysts prepared by 'wet' preparation methods, such as impregnation or deposition<sup>9</sup> displayed superior activities for both alcohol oxidation and hydrogen peroxide synthesis. It was noted that the high activity for hydrogen peroxide synthesis was practically limited by the high hydrogenation rates. In this paper we focus on the optimisation of the physically ground catalysts with the aim of improving metal dispersion, we show that the optimisation of the Au : Pd ratio and metal loading can lead to significantly different activities for alcohol oxidations. We demonstrate that significant enhancements of the TOF (turn over frequency) are achieved when the optimised catalysts are used.

#### Experimental

#### **Catalyst preparation**

**Physical grinding.** Palladium(II) acetate (Sigma Aldrich 99.9%) and gold(III) acetate (Alfa Aesar 99.9%) were added to the TiO<sub>2</sub> (Degussa, P25) and the mixture was ground manually in a pestle and mortar for 10 min. The mass of acetate salts used was varied to give 1–10 wt% total metal loading. Au : Pd metal ratio was varied, with 0:1, 1:4, 1:1, 4:1 and 1:0 being investigated. The resultant mixture was placed in a 4 inch ceramic boat and heat treated at 350 °C for 2 h in a tubular furnace under flowing helium (ramp rate 5 °C min<sup>-1</sup>).

**Impregnation.** Aqueous solutions of  $PdCl_2$  (Johnson Matthey, 6 mg in 1 mL) and  $HAuCl_4 \cdot 3H_2O$  (Johnson Matthey, 12.25 g in 1000 mL) were added to titania. The mixture was stirred for 5 min, until a paste was formed, dried at 110 °C for 16 h and calcined at 400 °C for 3 h in static air.

#### Catalyst testing

**Benzyl alcohol oxidation.** Catalyst testing was performed using a stainless steel autoclave (Autoclave Engineers In-line MagneDrive III) with a nominal volume of 100 mL and a maximum working pressure of 140 bar. The vessel was charged with benzyl alcohol (40 mL) and catalyst (25 mg). The autoclave was then purged three times with oxygen leaving the vessel at 10 bar. The pressure was maintained at a constant level throughout the experiment; as the oxygen was consumed in the reaction, it was replenished. The stirrer speed was set at 1500 r.p.m. and the reaction mixture was raised to the required temperature of 140 °C. Samples from the reactor were taken periodically *via* a sampling pipe, ensuring that the volume purged before sampling was higher than the tube volume, and analysed by GC (Varian 3800) using a CP-wax column.

Direct  $H_2O_2$  synthesis. Hydrogen peroxide synthesis and hydrogenation was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 mL and a maximum working pressure of 140 bar. To test each catalyst for  $H_2O_2$  synthesis, the autoclave was charged with catalyst (0.01 g) and 8.5 g solvent (5.6 g MeOH and 2.9 g  $H_2O$ ). The charged autoclave was then purged three times with 5%  $H_2/CO_2$  (7 bar) before filling with 5%  $H_2/CO_2$  to a pressure of 29 bar at 20 °C. The pressure was allowed to drop to 26 bar as the gas dissolved in the solvent at 20 °C. This was followed by the addition of 25%  $O_2/CO_2$  (11 bar). The temperature was then allowed to decrease to 2 °C followed by stirring (at 1200 rpm) of the reaction mixture for 30 min. The above reaction parameters represent the optimum conditions we have previously used for the synthesis of  $H_2O_2$ .  $H_2O_2$  productivity was determined by titrating aliquots of the final solution after reaction with acidified  $Ce(SO_4)_2$  (0.01 M) in the presence of two drops of ferroin indicator.

 $H_2O_2$  hydrogenation. Hydrogen peroxide hydrogenation was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 mL and a maximum working pressure of 140 bar. 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 CH<sub>3</sub>OH, 2.22 H<sub>2</sub>O and 0.68 g  $H_2O_2$  50% w/w). The charged autoclave was then purged three times with 5%  $H_2/CO_2$  (7 bar) before filling with 5%  $H_2/CO_2$ to a pressure of 29 bar at 20 °C. The temperature was then allowed to decrease to 2 °C followed by stirring (at 1200 rpm) the reaction mixture for 30 min. The amount of hydrogenated  $H_2O_2$  was determined by titrating aliquots with acidified  $Ce(SO_4)_2$  (0.0288 M) in the presence of a ferroin indicator.

Glycerol oxidation. Catalytic reactions were carried out using a 50 mL glass reactor. The glycerol solution (0.3 mol  $L^{-1}$ ) was admitted into the reactor with a solution of base (NaOH, substrate/base = 2) and the desired amount of catalyst (glycerol/metal mole fraction = 500) was suspended in the solution. The glass reactor was purged with oxygen three times and adjusted to the desired pressure of 3 bar. This pressure was maintained at a constant level throughout the experiment; hence as the oxygen was consumed in the reaction it was continuously replenished. The reaction mixture was heated to the desired temperature (60 °C) and stirred for the requisite amount of time (between 0.5 h and 4 h). The reactor vessel was then cooled to room temperature and the reaction mixture analysed. This analysis was carried out using high-pressure liquid chromatography (HPLC) equipped with ultraviolet and refractive index detectors. Reactants and products were separated using a Metacarb 67H column eluted with 0.01 mol  $L^{-1}$ aqueous H<sub>3</sub>PO<sub>4</sub> with a flow rate of 0.3 mL min<sup>-1</sup>. Samples of the reaction mixture (0.5 mL) were diluted (to 5 mL) using the eluent. Products were identified by comparison with authentic samples. For the quantification of the reactants consumed and products generated, an external calibration method was used.

#### Catalyst characterisation

**Powder X-ray diffraction.** Characterisation was performed using powder X-ray diffraction (XRD) on a  $(\theta-\theta)$  PANalytical X'pert Pro powder diffractometer using a Cu K<sub> $\alpha$ </sub> radiation source operating at 40 KeV and 40 mA. Standard analysis was performed using a 40 min scan with a back filled sample. Diffraction patterns of phases were identified using the ICDD data base. Diffraction patterns were analyzed using full pattern refinement, with background functions, zero shift and pseudo-Voigt profile functions. Reference crystal structure profiles were selected from the inorganic crystal structure database.

X-ray photoelectron spectroscopy. XPS measurements were made on a Kratos Axis Ultra DLD spectrometer using monochromatic Al  $K_{\alpha}$  radiation (120 W source power). An analyser pass energy of 160 eV was used for survey scans, while 40 eV was employed for detailed regional scans. Samples were mounted using double-sided adhesive tape, and binding energies were referenced as discussed in the text.

#### **Results and discussion**

Au and Pd catalysts were all prepared supported on titania as we have previously demonstrated it to be an extremely effective support for oxidation and reduction reactions.<sup>10,11</sup> Previously 2.5wt%Au + 2.5wt%Pd/TiO2 catalysts prepared by physical grinding (PG) were found to be more active than analogous catalysts prepared by either deposition precipitation (DP) or wet impregnation (IMP) for benzyl alcohol oxidation.<sup>21</sup> A study into the effect of metal ratio for impregnation prepared catalysts has shown that a gold : palladium ratio of 1:1 weight (~1:1.85 molar) afforded the catalysts with the highest initial activity for both alcohol oxidation (benzyl alcohol)<sup>22</sup> and the direct synthesis of hydrogen peroxide,<sup>23</sup> however when catalysts are prepared by the sol-immobilisation method and tested for glycerol oxidation a gold: palladium ratio of  $\sim 1:1.6$  weight (1:3 molar) was found to be the optimum.<sup>24</sup> It is clear from these results that for different preparation methods and different substrates the optimum metal ratio varies. To investigate the effect of Au: Pd ratio on the activity of physically ground catalysts for benzyl alcohol oxidation, several titania supported 5 wt% metal catalysts with varying Au : Pd ratios were prepared and tested. The results of these tests are shown in the time-on-line data presented in Fig. 1, with the corresponding selectivities to benzyaldehyde and toluene being shown in Fig. 2. A catalyst comprising of Pd only and a catalyst with a 1:4 Au:Pd composition had very similar benzyl alcohol conversion profiles and, as has been shown previously for impregnation catalysts,<sup>22</sup> the catalyst with a 1:1 Au: Pd ratio displayed the highest conversion. The catalysts comprised predominantly (4:1 Au:Pd) of Au had significantly lower conversion than the aforementioned catalysts. However, there was a clear synergistic effect demonstrated with the addition of only a small amount of palladium to the gold catalyst, after 3 h the 4%Au-1%Pd catalyst had converted over twice as much benzyl alcohol as the 5% Au catalyst. As all the catalysts tested comprised 5 wt% total metal and the Au: Pd ratio was varied the catalysts with the highest gold content will have the least number of mols of metal due to gold having almost twice the molar mass of palladium, therefore it is important to standardise the initial activity. The simplest way of standardising activity is by turn over frequency (TOF), Table 1 shows TOFs (mol substrate converted per mol of metal per hour) calculated at 0.5 h,



Fig. 1 The conversion of benzyl alcohol by catalysts (5 wt% metal) prepared by the physical grinding methodology with varying gold : palladium (weight) ratios.
5%Pd, ● 4%Pd-1%Au, ▲ 2.5%Pd-2.5%Au, ⋈ 1%Pd-4%Au, ■ 5%Au.



Fig. 2 The selectivity towards the major products during the oxidation of benzyl alcohol by catalysts (5 wt% metal) prepared by the physical grinding methodology with varying gold : palladium (weight) ratios. ▲ 5%Pd, ◆ 4%Pd-1%Au,
2.5%Pd-2.5%Au, 1%Pd-4%Au, ■ 5%Au. Filled symbols = toluene, open symbols = benzoic acid.

 Table 1
 The TOFs during the conversion of benzyl alcohol by catalysts (5 wt% metal) prepared by the physical grinding methodology with varying gold : palladium (weight) ratios

TOF (calculated at 0.5 h) $(h^{-1})$
34 164
30 892
42 156
27 958
18752



**Fig. 3** The selectivity at iso-conversion (30%) towards benzaldehyde and toluene by catalysts with various Au : Pd ratios. Black 5%Pd, dark grey 4%Pd–1%Au, light grey 2.5%Au–2.5%Pd, white 1%Pd–4%Au. The 5%Au catalysts did not reach 30% conversion in our experiments.

which emphasise the fact that a synergistic effect for gold palladium catalysts is observed when using the physical grinding preparation methodology. As previously observed for catalysts prepared by physical grinding and other techniques a monometallic Pd catalyst was significantly more active (TOF at 0.5 h of 34164  $h^{-1}$ ) than monometallic Au (TOF at 0.5 h of 18752 h<sup>-1</sup>).<sup>21</sup> However, the high activity of monometallic Pd catalysts can be partially attributed to the disproportionation reaction, as demonstrated by the poor selectivity towards benzaldehyde with significant selectivity towards toluene.<sup>25</sup> The 1:4 Au: Pd catalyst had only a slightly lower TOF, at 0.5 h (30 892  $h^{-1}$ ) than that observed for the monometallic Pd catalyst. This observation along with the comparably high selectivity towards toluene suggests that the dispersed active species is predominantly monometallic Pd in this catalyst. The rationale for this is that Au-Pd alloying is known to produce a synergistic effect on activity and partially inhibit disproportionation, neither of which were observed in this catalyst. The highest activity observed was that of the 1:1 Au: Pd catalyst (TOF at 0.5 h of 42156  $h^{-1}$ ), which also had the lowest toluene selectivity of all Pd containing catalysts. This clear synergistic effect is indicative of alloy formation, which has been confirmed from STEM analysis performed on a PG 1:1 Au:Pd catalyst used in the previous publication.<sup>21</sup> Interestingly the lower activity of the gold rich 4:1 Au: Pd catalyst relative to the 1:1 Au: Pd catalyst was also accompanied by an increase in toluene selectivity; this is again implicit of minimal alloying, with the Pd being in a monometallic state suggesting that extensive alloying between gold and palladium will only occur if the metals are present in a certain ratio range. To provide a fair comparison of the selectivites to benzaldeyde and toluene Fig. 3 shows the selectivities at 30% iso-conversion; the 5%Au catalyst is excluded from this comparison as the maximum activity reached was 27% in this study, however the remaining data emphasises the clear synergistic effect present in the 2.5%Au-2.5%Pd catalyst as discussed above.





Fig. 4 The conversion of benzyl alcohol by catalysts (1:1 weight Au: Pd) prepared by the physical grinding methodology with varying metal loading. ◆ 10 wt%, ● 5 wt%, ▲ 3 wt%, ⊠ 2.5 wt%, ■ 1 wt%.

In our previous work we extensively characterised the 5 wt% metal catalyst (1:1 Au:Pd) and we demonstrated that although very small bimetallic particles were formed, the vast majority of the metal was present as large (>50 nm) particles.<sup>21</sup> To try and obtain more effective metal distribution a series of catalysts with varying total metal loading were prepared, having the previously determined optimal 1:1 Au:Pd metal ratio. A comparison of 1:1 Au:Pd catalysts prepared with total loadings between 1 wt% and 10 wt% for the oxidation of benzyl alcohol is shown in Fig. 4. The highest conversion of benzyl alcohol was obtained with the 5 and 10 wt% catalysts, which have almost identical time-on-line profiles. As expected conversions then drop with lowering of metal loading. It is immediately apparent from this data is that the additional metal in the 10 wt% catalyst relative to the 5 wt% catalysts is providing no additional activity. To obtain greater clarity between the trends of metal loading and activity the TOFs, at 0.5 h reaction time, were calculated (Table 2). The previous observation made about the 10 wt% catalyst from the time-on-line data is confirmed by significant difference in TOFs calculated at 0.5 h, between the 10 wt% catalysts TOF of 18 395  $h^{-1}$  and the 5 wt% catalysts TOF of 42 156  $h^{-1}$ . The TOF of catalysts continued to increase as loading decreased up to the total 2.5 wt% metal catalyst demonstrating that even in the

 
 Table 2
 The TOFs during the conversion of benzyl alcohol by catalysts prepared by the physical grinding methodology with varying total metal loading and 1:1 Au:Pd (weight) ratio

Metal loading (Au : Pd 1 : 1 wt ratio)	TOF (calculated at 0.5 h) $(h^{-1})$
10	18 395
5	42 156
3	55 031
2.5	57 861
1	36 087

Table 3 XPS derived metal concentrations for the physically ground catalysts

Catalyst	% at conc Pd	% at conc Au	Pd/Au ratio
5%Au-5%Pd TiO <sub>2</sub>	2.94	0.28	10
2.5%Au-2.5%Pd TiO <sub>2</sub>	1.93	0.21	8.7
1.5%Au–1.5%Pd TiO <sub>2</sub>	1.34	0.11	11.7
1.25%Au-1.25%Pd TiO <sub>2</sub>	0.93	0.11	8.0
0.5%Au-0.5%Pd TiO <sub>2</sub>	0.29	n/a	n/a

5 wt% catalyst a significant amount of the metals are not effective for catalysis. There is a significant drop in the TOF for the 1 wt% catalyst however suggesting that this catalyst may contain metals in quantities below the minimum required for alloying to occur.

XPS analysis of the 1-10 wt% metal loaded catalysts was carried out and the results are shown in Table 3. In all cases the atomic surface concentration of gold was considerably lower than bulk concentration, while the surface concentration of palladium was relatively higher than the gold. This suggests, as we have previously reported, the distribution of palladium in these catalysts is significantly better than the distribution of gold. It was noted that no observable signal associated with gold was seen in the 1 wt% catalyst, explaining the drop in TOF as no dispersion of gold and hence no alloying was achieved. The calculated Pd:Au ratios for the catalysts with gold and palladium dispersion did not follow any discernible trend with ratios varying between 8 and 11.7. A high Pd: Au ratio can be indicative of a core shell structure to bimetallic nano particles however the Pd:Au ratios are considerably higher than those previously reported for catalysts prepared by the impregnation or deposition precipitation techniques9 suggesting it is a function of metal distribution rather than core shell formation as noted in our previous publication.9 Interestingly, the most active 2.5 wt% loaded catalyst clearly had the lowest Pd: Au ratio, showing a greater relative gold contribution and potentially indicating the greatest degree of alloy formation amongst the catalysts.

XRD patterns and subsequent refinement are shown in Fig. 5 and Table 4. A cubic phase with unit cell size that strongly matches that of gold was observed in all catalysts prepared with variable total weight loadings. The cubic

palladium was observed in all catalysts as well, with the exception of the lowest loaded 1 wt% catalyst. It was observed that, as total metal loadings increased, gold unit cell size decreased by a total of 0.2 Å<sup>3</sup> over the entire weight loading range. Conversely the palladium unit cell size increased slightly with increasing weight loading. These changes in unit cell size suggest some limited alloying, which increased with the metal weight loading. It should be noted that a unit cell size associated with bulk 1:1 Au:Pd was not observed in any samples indicating a system in which small incorporation of one element into another was prevalent. Average crystallite size of the gold rich phases was found to decrease from 165 nm in the 0.5%Au-0.5wt%Pd TiO<sub>2</sub> to 51 nm in the 5%Au-5wt%Pd TiO<sub>2</sub>, suggesting increased gold dispersion with increased metal loading. Alternatively palladium rich phases were found to have no variation in crystallite size, at ca. 12 nm, with changing weight loading. These observations corroborate those seen in XPS; expressly that gold disperses poorly with high concentration being required to achieve any significant dispersion and that palladium disperses significantly better, with concentration having a less obvious effect on dispersion. It is apparent that increasing palladium loading does little to affect its relative dispersion, therefore low loadings of this metal limit the effective wasting of metal. However, a minimum amount of gold appears necessary to facilitate its dispersion. Therefore samples with loadings around 1.25%Au-1.25%Pd TiO<sub>2</sub> appear to provide the best compromise with enough gold present to facilitate some dispersion and alloy formation and a low enough palladium concentration to minimise wasted metal.

We have previously shown that gold palladium catalysts are active for the oxidation of glycerol, therefore we tested the physically ground catalysts along with an analogous impregnation catalyst, the results of this testing are shown in Fig. 6. The amount of catalyst used in these experiments was varied in order to maintain a constant substrate: metal ratio of 500. It is interesting to note in the case of glycerol there seems to be two distinct trends, between the catalysts prepared by the impregnation method and the catalysts made by the physical grinding method. As the reactions were carried



Fig. 5 X-ray diffraction of Au-Pd TiO<sub>2</sub> (Au: Pd 1: 1) catalysts prepared by physical grinding with total metal loadings between 1–10 wt%. (a) 10 wt% Au-Pd TiO<sub>2</sub>, (b) 5 wt% Au-Pd TiO<sub>2</sub>, (c) 3 wt% Au-Pd TiO<sub>2</sub>, (d) 2.5 wt% Au-Pd TiO<sub>2</sub>, (e) 1 wt% Au-Pd TiO<sub>2</sub>

Catalyst	Metal phase	Unit cell volume (Å <sup>3</sup> )	Crystallite size (nm)	Weight fraction (%)	R value
5%Au-5%Pd TiO <sub>2</sub>	Au	67.70	51	3.2	2.5 (1.8)
-	Pd	59.03	10	5.3	( )
2.5%Au-2.5%Pd TiO <sub>2</sub>	Au	67.79	56	1.5	2.7 (1.9)
_	Pd	59.08	12	1.6	
1.5%Au–1.5%Pd TiO <sub>2</sub>	Au	67.85	98	0.7	2.9(2.0)
_	Pd	58.88	11	0.4	
1.25%Au-1.25%Pd TiO <sub>2</sub>	Au	67.86	144	0.4	2.7(2.0)
_	Pd	58.82	14	0.6	
0.5%Au-0.5%Pd TiO <sub>2</sub>	Au	67.94	165	0.1	2.9 (2.0)
-	Pd	n/a	n/a	n/a	( )

<sup>*a*</sup> Errors: unit cell volume  $\pm 0.1$  Å<sup>3</sup>, crystallite size  $\pm 2$  nm, weight fraction 10%.



**Fig. 6** The oxidation of glycerol by catalyst prepared by the physical grinding methodology (open symbols) and impregnation methodology (filled symbols) total metal loading:  $10\% \diamond$ ,  $5\% \Box$ ,  $3\% \triangle$ ,  $2.5\% \bigcirc$ , 2% —.

out at constant substrate : base ratio the TOFs in this case are directly proportional to the conversion. It is immediately clear that the catalysts prepared by the physical grinding method are considerably more active than those prepared by the impregnation method. Interestingly in contrast to the case of benzyl alcohol the metal loading does not seem to make a difference for glycerol oxidation, irrespective of the preparation method used. The selectivity towards C<sub>3</sub> products was lower for the physically ground catalysts, however this is most likely due to the activity of these catalysts and the reaction conditions used leading to over-oxidation of the desired products.

The trend found in the  $H_2O_2$  synthesis, for the catalysts prepared by physical grinding with 1–10 wt% metal loading (Fig. 7), was that of increasing  $H_2O_2$  productivity and hydrogenation. The notable exception being the lower productivity of the 10 wt% catalyst which indicates the additional metal is not beneficial for the direct synthesis of  $H_2O_2$ . To clarify these catalytic properties the results were calculated with respect to mass of metal as opposed to the conventional mass of catalyst (Fig. 8). The resulting trend is in



**Fig. 7**  $H_2O_2$  productivity and hydrogenation data for the 1 : 1 Au : Pd catalysts with various total metal loadings expressed in terms of mass of catalyst.  $\blacksquare$  Productivity,  $\diamond$  hydrogenation.



**Fig. 8**  $H_2O_2$  productivity and hydrogenation data for the 1:1 Au:Pd catalysts with various total metal loadings expressed in terms of mass of metal.  $\blacksquare$  Productivity,  $\diamond$  hydrogenation.

Paper

 Table 5
 The application of the physically ground catalysts to various substrates

Substrate	TOF (calculated at 0.5 h) $(h^{-1})$
Benzyl alcohol	25 079
Benzyl alcohol <sup>a</sup>	93 875
1-Phenylethanol	26 448
1,4-Butanediol	52 833
Cinnamyl alcohol <sup>b</sup>	1149

Reaction conditions: 40 mL of substrate, 160 °C, 14 mg 1.25% Au–1.25% Pd/TiO<sub>2</sub> catalyst, 10 bar O<sub>2</sub>.<sup>*a*</sup> 7 mg 2.5% Au–2.5% Pd/TiO<sub>2</sub> used as catalyst. <sup>*b*</sup> 40 mL 0.2 M aqueous solution, 90 °C.

concurrence with TOFs of the catalysts for benzyl alcohol oxidation, with the optimal loading for activity being 2.5 wt%. Evidence from catalytic testing is suggestive of increased metal dispersion, relative to total loading, as total metal loading is decreased. However, with both the oxidation of benzyl alcohol and  $H_2O_2$  synthesis activity dropped dramatically for the 1 wt% loaded catalyst, indicating a more complex change in catalyst properties with varying metal loading. The low productivity and decreased hydrogenation activity of the 10 wt% metal loaded catalyst indicates that the majority of the additional metal in this sample is not providing any activity.

Finally we carried out a series of tests to demonstrate the general applicability of the physically ground catalysts. It is clear from the previous data that the optimised loading for the highest activity with these catalysts is 1.25wt%Au–1.25wt%Pd. A series of catalytic oxidations were carried out on a range of substrates and the TOFs were calculated, these results are shown in Table 5. The TOF data presented demonstrates that these catalysts display high initial activities for a range of different oxidation substrates, the TOFs recorded for benzyl alcohol oxidation and cinnamyl alcohol (93 875 and 1149) are higher than those previously reported in the literature for either impregnation or deposition preparation methods demonstrating that by tuning the preparation method to obtain optimised catalysts significant enhancements in the activity of gold–palladium catalysed oxidations can be achieved.<sup>9,10</sup>

#### Conclusions

We have shown that further development of the physical grinding method of preparing chloride-free catalysts can lead to significant enhancements in the activity of the catalysts. By reducing the overall metal content of the catalyst higher TOFs can be achieved, indicating that in the higher loaded catalysts significant amounts of the metals deposited are 'spectators' to the active metal particles. It is also noted that if the total metal content is too low the synergistic effect of combining the two metals is lost, indicating that at low metal loadings the metals do not form the alloy particles that we believe to be responsible for the high activity of the catalyst. These observations from the catalytic data were confirmed by XRD and XPS characterisation. We have further shown the general applicability of this simple, scalable preparation method by demonstrating its ability to oxidise a variety of substrates with TOF that are comparable and occasionally better than those previously reported by other preparation methods.

## Note added after first publication

This article replaces the version published on 20th May 2013, in which Fig. 4 did not appear correctly. Additionally, Fig. 3 and Fig. 4 have been exchanged with one another, with respect to the previous version.

#### References

- 1 A. K. Sinha, S. Seelan, S. Tsubota and M. Haruta, *Angew. Chem.*, *Int. Ed.*, 2004, 43, 1546–1548.
- M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon,
  D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings,
  F. King, E. H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, 2005, 437, 1132–1135.
- 3 L. Kesavan, R. Tiruvalam, R. M. H. Ab, S. M. I. bin, D. I. Enache, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, S. H. Taylor, D. W. Knight, C. J. Kiely and G. J. Hutchings, *Science*, 2011, 331, 195–199.
- 4 S. Biella, L. Prati and M. Rossi, J. Catal., 2002, 206, 242-247.
- 5 F. Porta and L. Prati, J. Catal., 2004, 224, 397-403.
- 6 M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, 1987, 405-408.
- 7 M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, 115, 301–309.
- 8 P. Landon, P. J. Collier, A. J. Papworth, C. J. Kiely and G. J. Hutchings, *Chem. Commun.*, 2002, 2058–2059.
- 9 P. J. Miedziak, Q. He, J. K. Edwards, S. H. Taylor, D. W. Knight, B. Tarbit, C. J. Kiely and G. J. Hutchings, *Catal. Today*, 2011, 163, 47–54.
- D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu,
   A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely,
   D. W. Knight and G. J. Hutchings, *Science*, 2006, 311, 362–365.
- 11 J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely and G. J. Hutchings, *J. Catal.*, 2005, 236, 69–79.
- 12 A. Schulz and M. Hargittai, *Chem.-Eur. J.*, 2001, 7, 3657-3670.
- 13 H. S. Oh, J. H. Yang, C. K. Costello, Y. M. Wang, S. R. Bare, H. H. Kung and M. C. Kung, *J. Catal.*, 2002, 210, 375–386.
- 14 I. Dobrosz-Gomez, I. Kocemba and J. M. Rynkowski, *Appl. Catal., B*, 2009, **88**, 83–97.
- 15 H. H. Kung, M. C. Kung and C. K. Costello, *J. Catal.*, 2003, 216, 425-432.
- 16 F. Moreau, G. C. Bond and A. O. Taylor, J. Catal., 2005, 231, 105–114.
- 17 L. Delannoy, H. N. El, A. Musi, N. N. L. To, J.-M. Krafft and C. Louis, *J. Phys. Chem. B*, 2006, **110**, 22471–22478.
- 18 F. Somodi, I. Borbath, M. Hegedus, A. Tompos, I. E. Sajo, A. Szegedi, S. Rojas, F. J. L. Garcia and J. L. Margitfalvi, *Appl. Catal.*, A, 2008, 347, 216–222.
- 19 W.-C. Li, M. Comotti and F. Schueth, J. Catal., 2006, 237, 190–196.

- 20 Y. Lin, K. A. Watson, M. J. Fallbach, S. Ghose, J. G. Smith, D. M. Delozier, W. Cao, R. E. Crooks and J. W. Connell, ACS Nano, 2009, 3, 871–884.
- 21 S. A. Kondrat, G. Shaw, S. J. Freakley, Q. He, J. Hampton, J. K. Edwards, P. J. Miedziak, T. E. Davies, A. F. Carley, S. H. Taylor, C. J. Kiely and G. J. Hutchings, *Chem. Sci.*, 2012, 3, 2965–2971.
- 22 D. I. Enache, D. Barker, J. K. Edwards, S. H. Taylor, D. W. Knight, A. F. Carley and G. J. Hutchings, *Catal. Today*, 2007, 122, 407–411.
- 23 D. Enache, D. Knight and G. Hutchings, *Catal. Lett.*, 2005, 103, 43–52.
- 24 G. L. Brett, P. J. Miedziak, N. Dimitratos, J. A. Lopez-Sanchez, N. F. Dummer, R. Tiruvalam, C. J. Kiely, D. W. Knight, S. H. Taylor, D. J. Morgan, A. F. Carley and G. J. Hutchings, *Catal. Sci. Technol.*, 2012, 2, 97–104.
- 25 S. Meenakshisundaram, E. Nowicka, P. J. Miedziak,
  G. L. Brett, R. L. Jenkins, N. Dimitratos, S. H. Taylor,
  D. W. Knight, D. Bethell and G. J. Hutchings, *Faraday Discuss.*, 2010, 145, 341–356.