Selective formation of lactate by oxidation of 1,2-propanediol using gold palladium alloy supported nanocrystals

Nikolaos Dimitratos, Jose Antonio Lopez-Sanchez, Sankar Meenakshisundaram, Jinto Manjaly Anthonykutty, Gemma Brett, Albert F. Carley, Stuart H. Taylor, David W. Knight and Graham J. Hutchings*

Received 24th December 2008, Accepted 29th April 2009
First published as an Advance Article on the web 28th May 2009
DOI: 10.1039/b823285g

The use of bio-renewable resources, such as glycerol, a by-product from bio-diesel manufacture, can provide a viable way to make valuable products using greener technology. In particular, glycerol can be reduced to give 1,2-propanediol that can then be selectively oxidised to lactate, which has immense potential as a monomer for the synthesis of biodegradable polymers. We show that gold-palladium alloy catalysts can be very effective for the selective oxidation of 1,2-propanediol to lactate. Two supports, TiO_2 and carbon, and two preparation methods, wet impregnation and sol-immobilisation, are contrasted. The addition of palladium to gold significantly enhances the activity and retains the high selectivity to lactate using O_2 as oxidant (we observe 96% lactate selectivity at 94% conversion). Use of hydrogen peroxide is also possible but lower activities are observed as a result of the reaction conditions, but in this case no marked enhancement is observed on addition of palladium to gold. Comparison of the activity for C_3 alcohols shows that the reactivity decreases in the order: glycerol > 1,2-propanediol > 1,3-propanediol ~ 1-propanol > 2-propanol. The use of a sol-immobilisation preparation method as compared to impregnation leads to alloy catalysts with the highest activity for lactate formation from the oxidation of 1,2-propanediol; the origins of these activity trends are discussed.

Introduction

Lactic acid has the potential to become a major chemical for the production of biodegradable polymers. Until recently, lactic acid had relatively minor uses in a range of fine chemical applications. For example, in cosmetics it can be used as a moisturizer and is used in the textile industry as a mordant and also finds applications in tanning leather as well as in the manufacture of inks. It has uses in the foods industry, such as in yoghurt and cheese production. However, interest in lactic acid has recently been enhanced by the realisation that polylacetate is a biodegradable plastic, which has spurred the potential to transform lactic acid from being solely a fine chemical to being a commodity material, with annual production of >100 kt/annum.[1]

Lactic acid can be produced by number of chemical routes, *e.g.* by the reaction of acetaldehyde with HCN followed by hydrolysis with sulfuric acid, or by the reaction of CO with formadehyde in water at high pressures with HF as catalyst. As noted by Prati and Rossi,[2] these chemical processes are non-green. For this reason lactic acid is mainly produced by a fermentation process in which a range of carbohydrates are transformed, in the presence of calcium hydroxide, into calcium lactate that is readily recovered from the fermentation broth.[1] Lactic acid is then produced by reaction with an acid. The main problem with the fermentation route is the high dilutions required and the rate of production is very low and only dilute solutions can be produced as the enzyme is inhibited by the product. There is also a potential tension between carbohydrate utilisation as foodstuffs or plastics, although non-foodstuff carbohydrates can be used in the fermentation process. Hence the 'non-green' chemical routes can produce lactic acid at high rates, whereas the green fermentation route is hampered by the low productivity. There is therefore a need to identify a new green production strategy for the production of lactate and this is the topic that this paper addresses as selective oxidation of 1,2-propanediol presents a viable alternative pathway from a substrate that can be derived from a bio-renewable feedstock.

Recently, glycerol has been identified as a useful starting material for chemical synthesis.[3] Glycerol is a bio-renewable feedstock that is a by-product of the manufacture of bio-diesel,[4] and since there is an increasing drive towards greener fuels, the supply of glycerol as a sustainable raw material is growing steadily. Glycerol is an ideal substrate for the production of 1,2-propanediol by dehydration/hydrogenation,[5] and this can be linked to biodiesel production as 1,2-propanediol is used as an antifreeze. However, 1,2-propanediol is an ideal starting point for the synthesis of lactate using selective oxidation. T.Tsujino *et al.*[6] reacted aqueous 1,2-propanediol at 90 °C at pH 8 using Pd/C modified by Pb, Bi and/or Te as additives. They observed that both the primary and the secondary hydroxyl groups were reactive with their Pd/C catalysts and in addition to lactic acid, hydroxyacetone and pyruvic acid were also produced. Pyruvate was shown to be produced by sequential oxidation of lactate. Pinxt *et al.*[7] studied 1,2-propanediol oxidation using Pt/C modified by Pb, Bi and Sn and showed that pyruvate was produced

---

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, UK CF10 3AT.
E-mail: hutch@cardiff.ac.uk; Fax: +44 29 2087 4059; Tel: +44 29 2087 4059

in two parallel pathways from either lactate or hydroxyacetone. Under the conditions used by the authors, it is clear that with Pd or Pt catalysts only low selectivities of lactate are observed.

Supported gold catalysts have been shown to be very selective for a range of oxidation reactions.[8–11] In particular, they are effective for low temperature oxidation of CO,[12] even in the presence of H_2, H_2O and CO_2 a reaction that is finding some applications in fuel cells.[13,14] Gold has also been found to be effective for the selective oxidation of alkenes[15,16] and alcohols,[17] and for the selective hydrogenation of unsaturated carbonyl compounds and nitro groups.[18] Rossi and Prati were the first to show that supported gold nanoparticles were effective for alcohol oxidation in the presence of base.[2,19,20] Gold was found to be very selective for the oxidation of the primary alcohol group in diols and triols.[2,33,34] We have shown that, although gold alone is a very effective catalyst for the selective oxidation of an alcohol to an aldehyde under solvent-free conditions,[17] the alloying of gold with palladium leads to a twenty five-fold enhancement in activity with simultaneous retention of selectivity.[21] We have extended this work and have demonstrated that the combination of gold and palladium provides a pronounced synergistic effect in redox catalysis.[22–28] Furthermore, using a sol immobilisation preparation method affords even more reactive catalysts.[29,30] In this paper we investigate the synergistic effect of adding gold and palladium for the oxidation of 1,2-propanediol and demonstrate that very high selectivities to lactate can be obtained at high conversions.

Experimental

Catalyst preparation

The following notation is used for the catalyst samples we have prepared: I denotes impregnation, SI denotes sol-immobilisation, *w* denotes Au and Pd are present in a 1:1 ratio by weight, and *m* denotes Au and Pd are combined in a 1:1 molar ratio.

Impregnation method. Pd-only, Au-only and Au-Pd bimetallic catalysts were prepared by impregnation of carbon (Darco G60, Aldrich) and TiO_2 (Degussa, P25), *via* an impregnation method using aqueous solutions of $PdCl_2$ (Johnson Matthey) and/or $HAuCl_4.3H_2O$ (Johnson Matthey). Materials containing a total of 0.5, 1 and 5 wt% total metal were prepared and the Au and Pd were present in equal weights. For the 0.5%Au-0.5%Pd/carbon catalyst, the detailed preparation procedure employed is described below. An aqueous solution of $HAuCl_4{\cdot}3H_2O$ [2 ml, 5 g dissolved in water (250 ml)] and an aqueous solution of $PdCl_2$ [0.83 ml, 1 g in water (25 ml)] were simultaneously added to carbon (3.8 g). The paste formed was ground and dried at 110 °C for 16 h and calcined in static air, typically at 400 °C for 3 h.

Sol-immobilisation method. Au, Pd and Au-Pd catalysts supported on carbon or TiO_2 were also prepared using a sol-immobilisation method. An aqueous solution of $PdCl_2$ (Johnson Matthey) and $HAuCl_4{\cdot}3H_2O$ of the desired concentration was prepared. Polyvinyl alcohol (PVA) (1 wt% solution, Aldrich, weight average molecular weight M_W = 9,000–10,000 g/mol, 80% hydrolysed) was added (PVA/Au (wt/wt) = 1.2); a 0.1 M freshly prepared solution of $NaBH_4$ (>96%, Aldrich, $NaBH_4$/Au (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilised by adding activated carbon (acidified to pH 1 by sulfuric acid) under vigorous stirring conditions. The amount of support material required was calculated so as to have a total final metal loading of 1% wt. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water and dried at 120 °C overnight. Further catalysts were prepared using a 1:1 molar ratio of Au:Pd denoted as Au-Pd/TiO_{2SIm} and Au-Pd/C_{SIm}. Monometallic catalysts containing gold or palladium were also prepared using a similar methodology, and these are denoted Au/TiO_{2SI}, Pd/TiO_{2SI}, Au/C_{SI} and Pd/C_{SI} respectively.

Catalyst testing

Diol and alcohol oxidation

Autoclave reactor studies. Reactions were performed with a range of substrates: glycerol, 1,2-propanediol, 1,3-propanediol, 1-propanol and 2-propanol. Catalytic reactions were carried using a 50-mL Parr autoclave. The alcohol solution (0.6 M and NaOH/alcohol ratio = 2, mol/mol, 20 ml) was added into the reactor and the desired amount of catalyst (alcohol/metal ratio = 500–2000, mol/mol) was suspended in the solution. The autoclave was pressurised with oxygen (10 bar pressure) and heated at 60 °C. The reaction mixture was stirred at 1500 rpm for 4 h. The reactor vessel was cooled to room temperature and the reaction mixture was analysed by HPLC.

Glass reactor studies. Experiments were also conducted with hydrogen peroxide as oxidant at atmospheric pressure. In this case the alcohol solution (0.6 M and NaOH/alcohol molar ratio = 2, 20 ml) was placed in a round bottom flask (100 ml) and the desired amount of catalyst (alcohol/metal molar ratio = 2000) was suspended in the solution. Hydrogen peroxide was added (substrate/H_2O_2 molar ratio = 4) and the mixture was reacted at 60 °C, in air atmospheric pressure for 3h.

Product analysis. Analysis was carried out using HPLC with ultraviolet and refractive index detectors. Reactants and products were separated using a Metacarb 67H column. The eluent was an aqueous solution of H_3PO_4 (0.01M) and the flow was 0.45 ml/min. Samples of the reaction mixture (0.5 ml) were diluted (5 ml) using the eluent. Products were identified by comparison with authentic samples. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used and the calibration factor for each reactant/product was calculated. The substrate conversion and the selectivity to the reaction products were calculated on carbon basis. Furthermore the carbon mass balance was closed for the reactions reported within ±5%.

Results and discussion

For all the experiments we have selected catalysts that we have been characterised extensively in our previous studies using a combination of TEM, STEM-XEDS and XPS.[21,27,30,31] We aimed to contrast the reactivity of supported Au, Pd and Au-Pd nanocrystals made by impregnation and sol immobilisation for the selective oxidation of 1,2-propanediol. In addition we have selected two supports for evaluation (activated carbon and TiO_2). For the materials prepared by impregnation, the metal

Table 1 Effect of the metal composition and nature of support on the liquid phase oxidation of 1,2-propanediol with O_2 using Au and Pd catalysts synthesised by impregnation[a]

Catalyst	Conv. (%)	Selectivity (%) Lactate	Acetate	Formate	TOF (h^{-1}) [b]
1%Au/C_I	16	73.7	23.2	3.1	20
1%Pd/C_I	11	77.9	20.7	1.4	13
2.5%Au-2.5%Pd/C_{Iw}	32	95.4	4.0	0.7	40
1%Au/TiO_{2I}	15	80.9	17.7	1.4	18
1%Pd/TiO_{2I}	6	99.7	0.0	0.3	7
5%Au/TiO_{2I}	27	91.5	6.0	1.6	34
5%Pd/TiO_{2I}	3	92.0	7.5	0.5	4
2.5%Au-2.5%Pd/TiO_{2Iw}	91	96.3	3.6	0.1	114

[a] Reaction conditions: water (20 ml), 0.6 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 500, NaOH/1,2-propanediol molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 4 h. [b] TOF (h^{-1}) at 4 hours of reaction. TOF numbers were calculated on the basis of total loading of metals.

particle sizes ranged between 2 and 14 nm, with the average size being around 6 nm.[30] Occasional larger particles in excess of 25 nm were also present in this material, although these were relatively rare. By comparison, the metal particle size distribution in catalysts prepared by sol-immobilisation was found to be much narrower, *i.e.* between 4–7 nm.[30,35] For the impregnated materials the Au-Pd supported alloys have been characterised extensively by STEM-XEDS[21,27,30] and have been shown to have contrasting morphologies. The TiO_2-supported material, in common with other oxide-supported Au-Pd catalysts prepared by wet impregnation, have a core-shell structure with a palladium-rich shell and a gold-rich core, whereas the carbon-supported Au-Pd catalyst is a homogeneous alloy. We have recently found that the supported Au-Pd catalysts prepared using sol-immobilisation are also homogeneous alloys by using STEM-HAADF.[35] XPS analysis showed that the samples prepared by impregnation are almost entirely composed of Pd^{2+} species, whereas those prepared by sol-immobilisation contain both Pd^{2+} and Pd^0 With the latter predominating.[35] We consider that these two sets of well-characterised materials provide a useful basis for this study of the selective oxidation of 1,2-propanediol.

Comparison of Au, Pd and Au-Pd catalysts prepared by impregnation

We initially investigated the catalyst activity of mono-metallic TiO_2-supported catalysts prepared by wet impregnation comprising 5 wt% Au or Pd (Table 1) using standard reaction conditions in the presence of base. The main product was lactate and some minor amounts of acetate and formate were also observed. The Au/TiO_2 catalyst prepared by impregnation was considerably more active than the Pd/TiO_2 material. The selectivities were similar.

Au was markedly more reactive than Pd. For the carbon-supported catalysts, and again the selectivities were very similar, the main product being lactate. However, the carbon-supported catalysts prepared by impregnation were much less selective than the TiO_2-supported catalysts and in this case high quantities of acetate were observed. In addition, lower amounts of formate were also formed. The analysis was carried out using HPLC and the carbon mass balance was 100% and no CO_2 was observed.

The effect of loading amount of the metals was also investigated for the TiO_2-supported catalysts (Table 1). Using lower loadings of Au led to a lower conversion and selectivity for lactate, and we have previously observed a similar effect with glycerol oxidation.[32] In contrast the Pd catalyst gave a slightly higher conversion with an enhanced selectivity. These observations suggest that parallel pathways are operating for these products on these catalysts, and that specific sites may be separately responsible for lactate and acetate formation.

When Au and Pd are combined using the impregnation method, a significant enhancement in catalyst performance is observed and, in particular, the catalyst activity is improved whilst simultaneously increasing the selectivity for lactate, the desired product (Table 1). The effect is most pronounced for Au-Pd/TiO_{2Iw} where the catalyst activity is increased by a factor of *ca.* 3 when compared with the Au-only and by a factor of *ca.* 30 with the Pd-only catalysts. With Au-Pd/TiO_{2Iw}, after a reaction time of 4 h, 91% conversion was achieved with a selectivity of 96.3%.

The effect of the reaction time is shown for the 2.5%Au-2.5%Pd/TiO_{2Iw} and 2.5%Au-2.5%Pd/C_{2Iw} materials in Fig. 1.

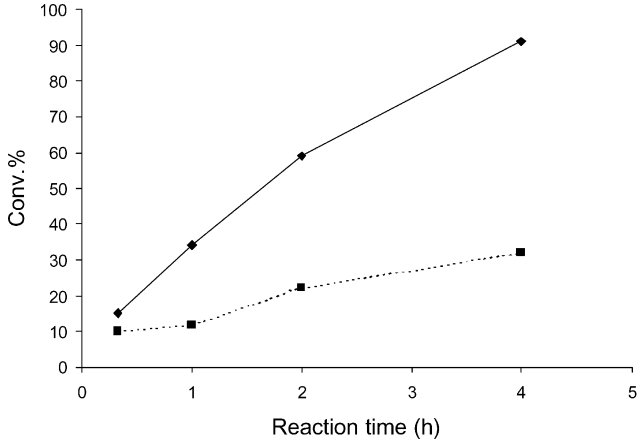


Fig. 1 Selective oxidation of 1,2-propanediol, ◆ 2.5wt%Au-2.5wt%Pd/TiO_{2Iw}; ■ 2.5wt%Au-2.5wt%Pd/C_{Iw}. Reaction conditions: water (20 ml), 0.6 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 500, NaOH/glycerol molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm.

It is clear that TiO_2 is the more effective support for Au-Pd alloys. This contrasts with the observations for the monometallic catalysts, although these can only be directly compared at lower loadings. The effect of time-on-line on selectivity is shown in Figs. 2 and 3. For the carbon-supported bimetallic catalyst (Fig. 2), the selectivity to lactate remains steady with reaction time (Fig. 2). For the TiO_2-supported catalyst (Fig. 3), the selectivity to lactate remains constant within experimental error, although it may be slightly lower at the very start of the reaction. These are key observations and indicate that the acetate and formate are formed in a parallel reaction pathway to lactate with these bimetallic catalysts. No pyruvate was observed at any reaction times with the bimetallic catalysts, indicating that lactate is very stable over these catalysts, a crucial observation for the design of a green synthetic process.

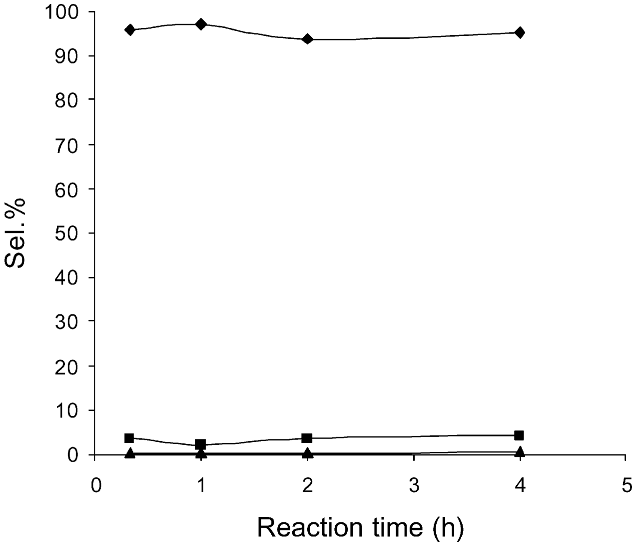


Fig. 2 Products formed in the oxidation of 1,2-propanediol using 2.5wt%Au-2.5wt%Pd/C_{Iw}. Reaction conditions as figure 1. Key: ♦ Lactate selectivity (%), ■ Acetate selectivity (%), ▲ Formate selectivity (%).

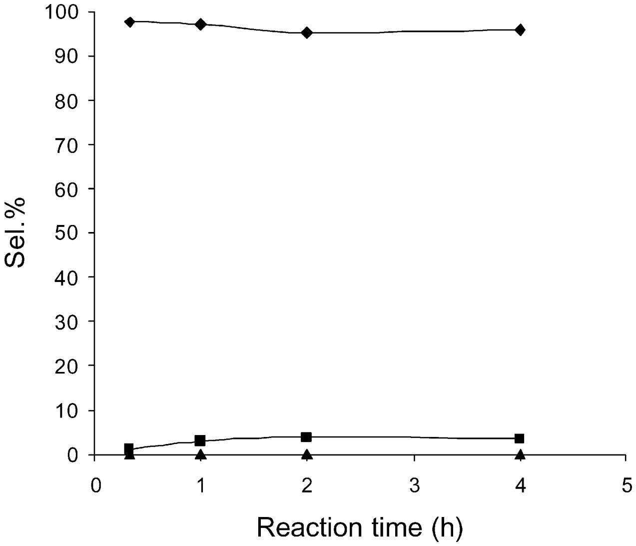


Fig. 3 Products formed in the oxidation of 1,2-propanediol using 2.5wt%Au-2.5wt%Pd/TiO_{2Iw}. Reaction conditions as figure 1. Key: ♦ Lactate selectivity (%), ■ Acetate selectivity (%), ▲ Formate selectivity (%).

Table 2 Catalytic activity of Au, Pd and Au-Pd supported catalysts prepared by sol-immobilisation in liquid phase oxidation of 1,2-propanediol with O_2[a]

		Selectivity (%)			
Catalyst	Conv. (%)	Lactate	Acetate	Formate	TOF (h^{-1})[b]
0.5%Au/TiO_{2SI}	58	96.0	4.0	0	1156
0.5%Pd/TiO_{2SI}	7	98.5	1.5	0	135
1%AuPd/TiO_{2SIm}	94	95.9	4.1	0	1880
1%Au/C_{SI}	31	92.0	7.2	0.8	619
1%Pd/C_{SI}	3	97.3	1.1	1.6	60
1%AuPd/C_{SIm}	53	99.3	0.3	0.5	1066

[a] Reaction conditions: water (20 ml), 0.6 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 2000, NaOH/1,2-propanediol molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 1 h. [b] TOF (h^{-1}) at 1 hour of reaction. TOF numbers were calculated on the basis of total loading of metals.

Comparison of Au, Pd and Au-Pd catalysts prepared by sol-immobilisation

A series of TiO_2- and carbon-supported catalysts were prepared using the sol-immobilisation technique and their activity for 1,2-propanediol oxidation under standard reaction conditions was contrasted with the catalyst prepared by wet impregnation (Tables 1 and 2). In the case of sol-immobilisation, much lower concentrations of the metals were used, since the method is restricted by the concentrations of the sols that can be prepared. Hence, catalysts containing 1 wt% of total metal have been prepared and evaluated. The catalysts prepared by the sol-immobilisation method are significantly more active for 1,2-propanediol oxidation than the equivalent sample prepared by wet impregnation. This effect is apparent for both the monometallic and the bimetallic materials. In general, a significant enhancement in activity by a factor of *ca.* 10–20 as determined on a mol basis is observed for all the catalysts. However, and most importantly, the selectivity to lactate is also enhanced. For 1%AuPd/TiO_{2SIm} after 1 h reaction a conversion of 94% was observed with a lactate selectivity of 95.9% and with 1%AuPd/C_{SIm} 53% conversion was observed with a selectivity of 99.3%. In both case only minor amounts of by-products were observed with the sol-immobilised catalysts.

Comparison of H_2O_2 and O_2 as oxidants

In a subsequent set of experiments, we have set out to contrast the catalyst performance using H_2O_2 as oxidant in place of molecular oxygen. H_2O_2 is considered to be a green oxidant, since the only by-product is water, and is often used as a more reactive form of oxygen; the results are shown in Table 3. For the monometallic catalysts prepared using impregnation, it is apparent that much lower selectivities to lactate are observed and higher amounts of acetate are apparent. However, this is not observed with the bimetallic AuPd catalysts prepared by impregnation, but in this case no synergistic enhancement in activity is observed. These results tend to suggest that the hydroperoxy species is not responsible for the selective formation of lactate, since this species would be expected to be formed and

Table 3 Liquid phase oxidation of 1,2-propanediol carried out at atmospheric pressure in the presence of hydrogen peroxide using Au and Pd supported catalysts[a]

		Selectivity (%)			
Catalyst	Conv. (%)	Lactate	Acetate	Formate	TOF (h^{-1}) [b]
5%Au/TiO_{2I}	6	82.6	14.5	2.9	40
5%Pd/TiO_{2I}	2	72.0	22.0	6.0	14
2.5%Au-2.5%Pd/C_{Iw}	3	100.0	0.0	0	21
2.5%Au-2.5%Pd/TiO_{2Iw}	0.4	100.0	0.0	0	3
1%Au/TiO_{2SI}	9	96.7	1.8	1.6	62[c]
1%Pd/TiO_{2SI}	8	97.8	1.2	1.0	54[c]
1%AuPd/TiO_{2SIm}	10	96.1	2.5	1.4	66[c]
1%(Au-Pd)/C_{SIm}	23	90.6	8.7	0.8	151[c]

[a] Reaction conditions: water (20 ml), 0.6 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 500, NaOH/1,2-propanediol molar ratio = 2, H_2O_2/1,2-propanediol molar ratio = 4, T = 60 °C, p(air) = 1 bar, reaction time = 3 h. [b] TOF (h^{-1}) at 3 hours of reaction. TOF numbers were calculated on the basis of total loading of metals. [c] 1,2-propanediol/total metal molar ratio = 2000.

the bimetallic catalysts prepared by impregnation are known to be highly active and selective for H_2O_2 synthesis[22–28,30] and alcohol oxidation to aldehydes.[21] In contrast to the catalysts made by impregnation, the catalyst made by sol immobilisation all show very high selectivity to lactate with H_2O_2 as oxidant, but again no synergistic enhancement in activity is observed for the bimetallic catalysts. Quantification of residual hydrogen peroxide at the end of reaction showed that it had been totally consumed, in agreement with previous reported data.[36]

Effect of the substrate on reactivity

To examine the effect of the substrate structure on reactivity, we have examined the reactions of a range of C_3 alcohols using a catalyst prepared by sol immobilisation that has been found to be the most active and selective (1%AuPd/TiO_{2SIm}); the results are shown in Table 4. Using O_2 as the oxidant, for the primary alcohols we observed very high selectivities to the mono-acid and for 2-propanol, acetone was selectively, if more slowly formed; the complete order of reactivity observed is shown in Scheme 1. With H_2O_2 as oxidant, the order of reactivity was different: with this oxidant, 1,3-propanediol was much less reactive.

The observed order of reactivity with O_2 as oxidant is somewhat puzzling, given the significant preference for this catalyst system to oxidise primary alcohols at the expense of secondary alcohols; hence, one would expect 1,3-propanediol to show similar reactivity to glycerol, as both have two primary alcohol groups. That it does not (Scheme 1) suggests that the otherwise relatively unreactive secondary hydroxyl, which is present in glycerol but not in 1,3-propanediol, promotes the oxidation in some way. This could be due to some form of anchiomeric assistance, for example by intramolecular hydrogen bonding between the proton of the secondary hydroxyl group and the presumed alkoxide, which is initially formed from the primary alcohol prior to its oxidation. Alternatively, the vicinal diol system would be much more capable of forming a complex with the catalyst metal surface, which could facilitate oxidation. Further, the electron withdrawal by the secondary hydroxyl oxygen could weaken the C-H bond, which has to be broken during oxidation of the primary hydroxyl. Such an effect could be considerable, as such bond cleavage could be a rate determining step.

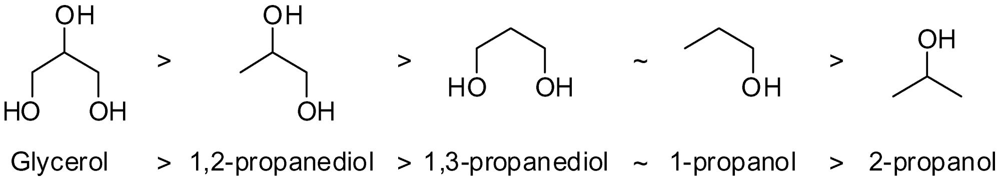
Effect of the concentration of NaOH

The effect of the concentration of NaOH was investigated for both O_2 and H_2O_2 as oxidants (Table 5). Increasing the concentration increased the conversion and selectivity for lactate.

Table 4 Effect of the substrate structure and oxidant using 1% wt.Au-Pd/TiO_2 catalyst prepared by sol-immobilisation

Substrate	Oxidant	Conv. (%)	Selectivity (%)	TOF (h^{-1})
Glycerol	O_2 [a]	100	61.3 (Glycerate)	1999[c]
1,2-propanediol	O_2 [a]	94	95.9 (Lactate)	1880[c]
1,3-propanediol	O_2 [a]	62	94.9 (3-hydroxy-propanoate)	1246[c]
1-propanol	O_2 [a]	62	100.0 (propanoate)	1239[c]
2-propanol	O_2 [a]	35	100.0 (acetone)	691[c]
Glycerol	H_2O_2 [b]	13	53.5 (Glycerate)	83[d]
1,2-propanediol	H_2O_2 [b]	10	95.6 (Lactate)	66[d]
1,3-propanediol	H_2O_2 [b]	3	100.0 (3-hydroxy-propanoate)	17[d]
1-propanol	H_2O_2 [b]	19	100.0 (propanoate)	125[d]
2-propanol	H_2O_2 [b]	14	100.0 (acetone)	93[d]

[a] Reaction conditions: water (20 ml), 0.6 M Substrate, Substrate/total metal molar ratio = 2000, NaOH/Substrate molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 1 h. [b] Reaction conditions: water (20 ml), 0.6 M Substrate, Substrate/total metal molar ratio = 2000, NaOH/Substrate molar ratio= 2, H_2O_2/1,2-propanediol molar ratio = 4, T = 60 °C, p(air) = 1 bar, reaction time = 3 h. [c] TOF (h^{-1}) at 1 hour of reaction. TOF numbers were calculated on the basis of total loading of metals. [d] TOF (h^{-1}) at 3 hour of reaction. TOF numbers were calculated on the basis of total loading of metals.



Scheme 1

Table 5 Influence of NaOH/1,2 propanediol molar ratio in the liquid phase oxidation of 1,2-propanediol with 1%Au/C_{SI}

NaOH/M molar ratio	Conv. (%)	Selectivity (%) Lactate	Acetate	Formate	TOF (h^{-1})
0.5[a]	15	81.0	18.4	0.6	295[c]
1[a]	21	88.0	10.7	0.5	420[c]
2[a]	31	92.0	7.2	0.8	619[c]
4[a]	23	95.7	3.3	1.0	463[c]
0.5[b]	6	80.8	0.8	18.4	37[d]
1[b]	7	73.5	1.6	24.9	49[d]
2[b]	8	89.2	0.6	10.2	57[d]
4[b]	19	84.3	3.0	12.6	124[d]

[a] Reaction conditions: water (20 ml), 0.3 M Substrate, Substrate/total metal molar ratio = 2000, NaOH/Substrate molar ratio = 0.5–4, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 1 h. [b] Reaction conditions: water (20 ml), 0.3 M 1,2-propanediol, 1,2-propanediol/total metal molar ratio = 2000, NaOH/1,2-propanediol molar ratio = 0.5–4, H_2O_2/1,2-propanediol molar ratio = 4, T = 60 °C, p(air) = 1 bar, reaction time = 3 h. [c] TOF (h^{-1}) at 1 hour of reaction. TOF numbers were calculated on the basis of total loading of metals. [d] TOF (h^{-1}) at 3 hours of reaction. TOF numbers were calculated on the basis of total loading of metals.

Table 6 Oxidation of intermediates (hydroxyacetone, pyruvaldehyde and pyruvic acid) using 1%Au/C_{SI}

Substrate	Conv. (%)	Selectivity (%)[a] Lactate	Acetate	Formate
Hydroxyacetone[b]	100	84.0	15.4	0.6
Hydroxyacetone[c]	100	69.9	26.6	3.5
Pyruvaldehyde[b]	100	100	0	0
Pyruvaldehyde[c]	100	100	0	0
Pyruvic acid[b]	0	0	0	0
Pyruvic acid[c]	31	0	100	0

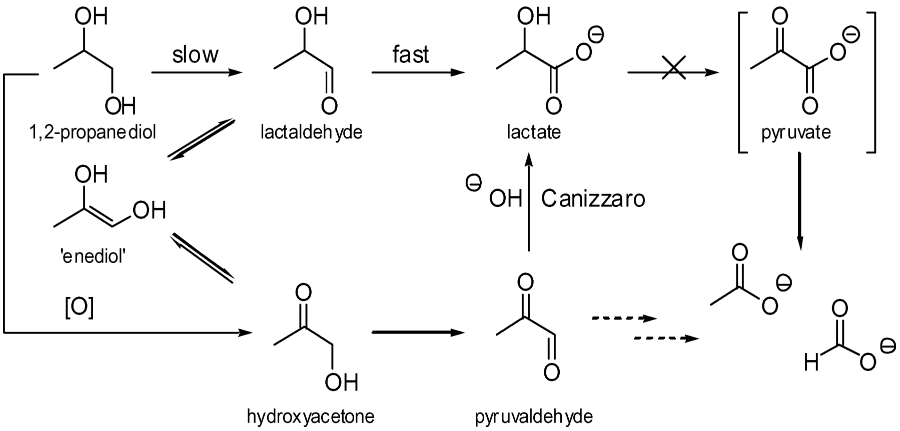
[a] Analysis excluding carbon oxides, which may be formed in addition. [b] Reaction conditions: water (20 ml), 0.3 M Substrate, Substrate/total metal molar ratio = 2000, NaOH/Substrate molar ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 0.5 h. [c] Reaction conditions: water (20 ml), 0.3 M Substrate, Substrate/total metal mol ratio = 2000, NaOH/Substrate mol ratio = 2, T = 60 °C, pO_2 = 10 bar, stirring rate 1500 rpm, reaction time = 1 h.

With H_2O_2, the effect was primarily on conversion whereas for O_2 the use of 2M NaOH was found to be optimal, although acceptable rates were achieved with O_2 as oxidant with lower NaOH concentrations.

Comments on the mechanism of product formation

It is apparent that the oxidation of alcohols using the bimetallic AuPd catalysts is very selective for the formation of mono-acid products, even when additional oxidations are possible. The reactivity patterns we have observed for the C_3 alcohols are consistent with their regiochemistry and the propensity of these catalysts to oxidise primary alcohols. In addition, for 1,2-propanediol, by-product generation (acetate and formate) suggests that parallel pathways may be operating. In addition, when H_2O_2 is used as the oxidant, no synergistic enhancement in activity is observed, suggesting that a hydroperoxy species may not be the selective oxidation species present on the surface of the very active catalysts.

The most selective catalyst system discovered during the present work would appear to operate in a very straightforward fashion, by reason of the very high regioselectivity: oxidation of 1,2-propanediol to lactaldehyde is presumably overall a slow step, which is followed by a relatively fast second oxidation to the observed lactate product (Scheme 2). Further oxidation to pyruvate is not observed, but may occur (see Table 6), even



Scheme 2

with less selective systems, in line with previously reported observations.

However, in less selective or less effective reactions, when the major by-product was very largely acetate, other pathways must be involved or any pyruvate formed is being rapidly transformed into acetate (Table 6). Although not observed during the present work, this may also feature the intermediacy of hydroxyacetone, formed either by direct oxidation of 1,2-propanediol or, more likely, by base-induced tautomeric equilibrium with the intermediate enediol derived from lactaldehyde. That the final lactate product is stable with respect to oxidation to pyruvate supports the contention that these catalyst systems are quite unreactive with secondary alcohols and hence it seems unlikely that oxidation of 1,2-propanediol to hydroxyacetone would be an important contributor to this chemistry (see Scheme 2). Subsequent oxidation of hydroxyacetone to pyruvaldehyde, which was also not detected, would now be viable and could then lead to more lactic acid by a Cannizzaro reaction,[2] as well as to both acetate and formate by oxidative cleavage. In the absence of reliable and detailed knowledge of the true nature of the intermediates involved in these oxidations, we cannot comment further on the reaction mechanism. However, we have carried out some initial studies using hydroxyacetone, pyruvaldehyde and pyruvic acid under the same reaction conditions in the presence of NaOH at 60 °C (Table 6). Pyruvaldehyde reacted immediately on addition of base to form lactate exclusively. This tends to explain why the former was not detected but does not confirm it as a central intermediate in the formation of lactate. This is wholly consistent with earlier proposals.[2,7] Hydroxyacetone also reacted immediately on addition of NaOH to the reaction mixture. However, although lactate was the major product, significant quantities of acetate and formate were also formed. This indicates that the route based on hydroxyacetone can also be a route for the formation of acetate and formate that are observed as products. In contrast, pyruvic acid was less reactive and reaction in the presence of catalyst led to the formation of acetate. In this case no formate was observed, but the carbon mass balance was low and we suspect that carbon oxides are also formed. Further work will be carried out to unravel these mechanistic complexities.

Conclusions

We have shown that AuPd catalysts prepared using a sol immobilisation method are very active for the selective oxidation of 1,2-propanediol to lactate. The sol immobilised materials are significantly more active than catalysts prepared by impregnation and this is due to the smaller metal particle sizes attained with the sol immobilisation method Alloying gold with palladium has also been shown to improve activity, and in some instances even to enhance selectivity to lactic acid. Very high selectivities at high conversion are achieved. This is possible because the formation of lactate and the by-products, acetate and formate, occurs *via* parallel reaction pathways. In view of this, we consider that this selective oxidation pathway forms the basis of a new green process for lactate synthesis, which could compete with the present fermentation pathway.

Acknowledgements

This work formed part of the Glycerol Challenge and Sasol and the Technology Strategy Board are thanked for their financial support. This project is co-funded by the Technology Strategy Board's Collaborative Research and Development programme, following an open competition. The Technology Strategy Board is an executive body established by the Government to drive innovation. It promotes and invests in research, development and the exploitation of science, technology and new ideas for the benefit of business – increasing sustainable economic growth in the UK and improving quality of life. For more information visit www.innovateuk.org.

References

1 R. Datta and M. Henry, *J. Chem. Technol. Biotechnol.*, 2006, **81**, 1119.
2 L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552.
3 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411.
4 G. W. Huber and A. Corma, *Angew. Chem. Int. Ed.*, 2007, **46**, 7184.
5 T. Miyazawa, Y. Kasunoki, K. Kunimori and K. Tomisihige, *J. Catal.*, 2006, **240**, 213.
6 T. Tsujino, T. Ohigashi, S. Sugiyama, K. Kawashiro and H. Hayashi, *J Molec. Cat.*, 1992, **71**, 25.
7 H. H. C. M. Pinxt, B. F. M. Kuster and G. B. Marin, *Appl. Catal. A*, 2000, **191**, 45.
8 A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem. Int. Ed.*, 2006, **45**, 7896.
9 G. C. Bond and D. T. Thompson, *Catal. Rev.-Sci. Eng.*, 1999, **41**, 319.
10 A. Corma and H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096.
11 C. Della, Pina, E. Falletta, L. Prati and M. Rossi, *Chem. Soc. Rev.*, 2008, **37**, 2077.
12 M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, 1987, **16**, 405.
13 P. Landon, J. Ferguson, B. E. Solsona, T. Garcia, A. F. Carley, A. A. Herzing, C. J. Kiely, S. E. Golunski and G. J. Hutchings, *Chem. Commun.*, 2005, 3385.
14 P. Landon, J. Ferguson, B. E. Solsona, T. Garcia, S. Al-Sayari, A. F. Carley, A. Herzing, C. J. Kiely, M. Makkee, J. A. Moulijn, A. Overweg, S. E. Golunski and G. J. Hutchings, *J. Mat. Chem.*, 2006, **16**, 199.
15 A. K. Sinha, S. Seelan, S. Tsubota and M. Haruta, *Angew. Chem. Int. Ed.*, 2004, **43**, 1546.
16 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.
17 A. Abad, P. Conception, A. Corma and H. Garcia, *Angew. Chem. Int. Ed.*, 2005, **44**, 4066.
18 A. Corma and P. Serna, *Science*, 2006, **313**, 332.
19 F. Porta, L. Prati, M. Rossi and G. Scari, *J. Catal.*, 2002, **211**, 464.
20 F. Porta and L. Prati, *J. Catal.*, 2004, **224**, 397.
21 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.
22 P. Landon, P. J. Collier, A. J. Papworth, C. J. Kiely and G. J. Hutchings, *Chem. Commun.*, 2002, 2058.
23 P. Landon, P. J. Collier, A. F. Carley, D. Chadwick, A. J. Papworth, A. Burrows, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1917.
24 B. E. Solsona, J. K. Edwards, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely and G. J. Hutchings, *Chem. Mater.*, 2006, **18**, 2689.
25 J. K. Edwards, B. Solsona, P. Landon, A. F. Carley, A. Herzing, M. Watanabe, C. J. Kiely and G. J. Hutchings, *J. Mater. Chem.*, 2005, **15**, 4595.
26 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.

27 J. K. Edwards, A. F. Carley, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *Faraday Disc.*, 2008, **138**, 225.

28 J. K. Edwards, A. Thomas, A. F. Carley, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *Green Chem.*, 2008, **10**, 388.

29 N. Dimitratos, J. A. Lopez-Sanchez, D. Morgan, A. F. Carley, L. Prati and G. J. Hutchings, *Cat. Today*, 2007, **122**, 317.

30 J. A. Lopez-Sanchez, N. Dimitratos, P. Miedziak, E. Ntainjua, J. K. Edwards, D. Morgan, A. F. Carley, R. Tiruvalam, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1921.

31 A. A. Herzing, M. Watanabe, J. K. Edwards, M. Conte, Z.-R. Tang, G. J. Hutchings and C. J. Kiely, *Faraday Disc.*, 2008, **138**, 337.

32 S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1329.

33 S. Carrettin, P. McMorn, P. Johnston, K. Griffin and G. J. Hutchings, *Chem. Commun.*, 2002, 696.

34 S. Demirel, P. Kern, M. Lucas and P. Claus, *Catal. Today*, 2007, **122**, 292.

35 N. Dimitratos, J. A. Lopez-Sanchez, J. M. Anthonykutty, A. F. Carley, R. C. Tiruvalam, A. A. Herzing, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Phys. Chem. Chem. Phys.*, 2009, DOI: 10.1039/b904317a.

36 L. Prati, P. Spontoni and A. Gaiassi, *Topics in Catalysis*, 2009, **52**, 288.